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BOSTON UNIVERSITY
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THESIS

REDUCING AGENTS IN VOLUMETRIC ANALYSIS

WITH SPECIAL REFERENCE TO

STANNOUS PERCHLORATE

Waldemar Stanwood McGuire

(B.S., Massachusetts Institute of Technology, 1918)

In partial fulfilment of the requirements of the degree of
MASTER of ARTS

1930

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The author wishes to acknowledge his indebtedness to Professor Edward O. Holmes, Jr., of the Department of Chemistry, without whose helpful suggestions and kindly criticisms, this thesis would not have been possible.

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Summary

Bibliography

1. The first thing I noticed
2. when I stepped out of the plane
3. was the fresh air. It felt like
4. I had been in a bubble for
5. hours. The sun was shining
6. brightly, and the birds were
7. singing. It was a beautiful
8. sight. I had never seen
9. anything like this before.
10. I was in good luck. I had
11. found a new home. I was
12. happy. I was free. I was
13. alive. I was home.

14. I was home.

INTRODUCTION

The processes of Volumetric Analysis may be grouped into three classes, as Neutralization processes, such as that between Sodium Hydroxide and Hydrochloric Acid; Precipitation processes, such as that between Sodium Chloride and Silver Nitrate; and Oxidation-Reduction processes, such as that between Ferrous Chloride and Potassium Permanganate. Some authors, however, group the first two types together as those in which no change in valence takes place, as opposed to the remaining class in which there are always at least two such changes.

Neutralization processes were among those first developed in Analytical Chemistry as in 1839¹ we find Potassium Carbonate recommended as a primary standard; thus some progress must have been made already in this direction. Lunge² in 1878, proposed the substitution of Methyl Orange, an artificially prepared dyestuff, in place of the various natural extracts previously used, thus initiating a technical development which has only recently been completed by the work of Clark³ and others. Hildebrand's⁴ introduction of the Hydrogen electrode in 1913 for use in titration furnished another means of obtaining the endpoint. As a result of the present high development of these colorimetric and potentiometric methods to all sorts of neutralizations, it is doubtful whether we may expect much further

1. Ure, Dictionary of Arts, (1839)
2. G. Lunge, Ber. 11, 1944 (1878)
3. W. M. Clark, The Determination of Hydrogen Ions (1928)
4. J. H. Hildebrand, J. Am. Chem. Soc., 35, 869 (1913)

The progress of knowledge in the field of the history of the United States has been rapid and steady. The discovery of the first human remains in the United States was made in 1801, when the bones of a man were found in the cave of the Indians at the mouth of the Ohio River. Since that time, the discovery of human remains has been a constant feature of the history of the United States. The discovery of the first human remains in the United States was made in 1801, when the bones of a man were found in the cave of the Indians at the mouth of the Ohio River. Since that time, the discovery of human remains has been a constant feature of the history of the United States.

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progress in that direction.

The idea of Volumetric Precipitating processes probably originated with Gay-Lussac⁵ for in 1828 he suggested a method of determining Sulfate with a Barium Solution, and in 1832 published the method for Silver determination which bears his name⁶. Numerous procedures have been suggested since that time, but up to the present very few have been found of any value, principally due to the difficulty of obtaining the correct endpoint, by means of the indicators available. While theoretically conductometric methods of obtaining it could be used at present little has been accomplished. It is probable that the recent work of Fajans⁷ and Hassel involving the use of "absorption" indicators will open up a broad field for the further advancement of this type of Volumetric Analysis.

By far the largest number of Volumetric processes are included in the third group, since many of our commonly determined elements are capable of variable valence or of combining with other elements which possess this property. It might seem that by this method the compounds of any two elements of variable valence could be used as the necessary oxidizing and reducing materials. The exact choice of materials is limited, however, by the necessity of choosing them with regard to proper oxidation potentials* as well as to the practical avoidance of

5. J. L. Gay-Lussac, *Ann. chim. phys.*, 39, 352 (1828)
6. J. L. Gay-Lussac, *Instruction sur l'essai des matieres d'argent par la voie humide.* (1832)
7. K. Fajans and O. Hassel, *Z. Elektrochem.*, 29, 495 (1924)
- *. See Chapter I

progress in this direction.

The idea of Voluntary Translocation of the Process

originated with Gay-Lussac, but in 1855 he suggested a method

of determining relative rates with a Barium solution, and in 1857

published the method for Silver determination which bears his

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Principally due to the difficulty of obtaining the correct

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the recent work of Tjarks and Hassel involving the use of

"radioactive" indicators will open up a broad field for the

future advancement of this type of Voluntary Translocation.

But for the present number of Voluntary Translocation with the

added in the third group, elements of our common belief

and elements are capable of variable valence or of combining

with other elements which possess this property. It might

now that by this method as compared of any two elements of

variable valence could be used as the necessary oxidizing and

reducing medium. The exact choice of material is limited,

however, by the necessity of combining with water to form

stable compounds, as well as to the practical availability of

1. J. Gay-Lussac, Ann. Chim. Phys., 35, 257 (1807)
2. J. Gay-Lussac, Trans. Phil. Soc. London, 1808
3. J. Gay-Lussac, Ann. Chim. Phys., 35, 257 (1807)
4. J. Gay-Lussac, Ann. Chim. Phys., 35, 257 (1807)
5. J. Gay-Lussac, Ann. Chim. Phys., 35, 257 (1807)
6. J. Gay-Lussac, Ann. Chim. Phys., 35, 257 (1807)
7. J. Gay-Lussac, Ann. Chim. Phys., 35, 257 (1807)
8. J. Gay-Lussac, Ann. Chim. Phys., 35, 257 (1807)
9. J. Gay-Lussac, Ann. Chim. Phys., 35, 257 (1807)
10. J. Gay-Lussac, Ann. Chim. Phys., 35, 257 (1807)

errors such as would result from the use of unsuitable indicators or to the occurrence of side reactions.

Dupasquier⁸ in 1840 carried out the first method involving oxidation and reduction when he titrated Iodine with Sulfurous Acid. Schwarz⁹ in 1853 introduced the use of Sodium Thiosulfate along with the Iodine, and since that time the applications of these useful solutions have been increasing constantly. Later other well known oxidizing agents such as Potassium Permanganate, Potassium Bichromate, Potassium Iodate, and Potassium Bromate were introduced as well as Oxalic Acid, Arsenious Acid, Ferrous and Stannous salts which are reducing agents. While in Starch we have a suitable indicator for the Iodine-Thiosulfate reaction, we had until recently none for the others, except for the Permanganate, which acts for its own indicator.

With the application of potentiometric methods as recommended by Hildebrand* and the development of suitable oxidation-potential indicators by Clark¹⁰ other materials have been developed, as for example, in the recent work of Willard¹¹ with Ceric salts; and in all probability the next few years will see many others.

It is the purpose of this investigation to first consider

8. Dupasquier, Ann. chim. phys., 73, (1840)
9. Schwarz, Anleitung sur Massanalyse. (1853)
- * See Ref. 4 page 1
10. W. M. Clark and others, Pub. Health Reports 38, 443 (1923) 38, 666 (1923) etc.
11. H. H. Willard, J. Am. Chem. Soc., 50, 1222, 1334, 1368, 1372, 1379, (1928)

errors such as would result from the use of uncalibrated
 devices or the occurrence of other reactions.
 On the other hand, in 1946 carried out the first method of
 direct oxidation and reduction when he obtained iodine with
 hydrogenous acid. However, in 1953 introduced the use of iodine
 trichloride along with the iodine, and since that time the
 applications of these reagent solutions have been increasing.
 Later work has shown existing errors such as
 presence of hydrogen peroxide, presence of hydrogen
 and its reaction with iodine were introduced as well as other acids,
 arsenic acid, ferric and stannous acids which are reducing
 agents. While in 1954 we have a reliable indicator for
 iodine-trichloride reaction, we had until recently none for
 the other, except for the ferrous ion, which acts for the
 own indicator.

With the application of potentiometric methods as re-
 commended by Hildebrand and the development of accurate
 oxidation-potential indicators by Clark, other methods
 have been developed, as for example, in the recent work of
 Pittard, with ceric salts; and in all probability the new
 methods will see many others.

It is the purpose of this paper to review the literature in this field.

1. H. Hildebrand, and others, *Anal. Chem.*, 25, (1949)
2. H. Hildebrand, *Anal. Chem.*, 25, (1949)
3. H. Hildebrand, *Anal. Chem.*, 25, (1949)
4. H. Hildebrand, *Anal. Chem.*, 25, (1949)
5. H. Hildebrand, *Anal. Chem.*, 25, (1949)
6. H. Hildebrand, *Anal. Chem.*, 25, (1949)
7. H. Hildebrand, *Anal. Chem.*, 25, (1949)
8. H. Hildebrand, *Anal. Chem.*, 25, (1949)
9. H. Hildebrand, *Anal. Chem.*, 25, (1949)
10. H. Hildebrand, *Anal. Chem.*, 25, (1949)
11. H. Hildebrand, *Anal. Chem.*, 25, (1949)
12. H. Hildebrand, *Anal. Chem.*, 25, (1949)

the general principles underlying the use of Volumetric reducing agents in general, second to summarize the advantages of, and objections to, those commonly used at present, and third to investigate the possibilities for the use of Stannous Perchlorate in this direction.

Stannous Perchlorate, $\text{Sn}(\text{ClO}_4)_2$, is a white crystalline solid, soluble in water and in concentrated hydrochloric acid. It is a strong reducing agent, and is used in the determination of iron, copper, and other metals. It is also used in the synthesis of organic compounds. The use of Stannous Perchlorate as a reducing agent is based on the fact that it is easily oxidized to Stannous Chloride, SnCl_2 , which is a stable compound. The reaction is as follows:

$$\text{Sn}(\text{ClO}_4)_2 + 2\text{H}^+ \rightarrow \text{SnCl}_2 + 2\text{HClO}_4$$

The use of Stannous Perchlorate as a reducing agent is based on the fact that it is easily oxidized to Stannous Chloride, SnCl_2 , which is a stable compound. The reaction is as follows:

$$\text{Sn}(\text{ClO}_4)_2 + 2\text{H}^+ \rightarrow \text{SnCl}_2 + 2\text{HClO}_4$$

1. E. J. Meehan, *Anal. Chem.* 34, 171 (1962).
2. E. J. Meehan, *Anal. Chem.* 34, 171 (1962).
3. E. J. Meehan, *Anal. Chem.* 34, 171 (1962).
4. E. J. Meehan, *Anal. Chem.* 34, 171 (1962).
5. E. J. Meehan, *Anal. Chem.* 34, 171 (1962).

the general principles underlying the use of Verbalis in the
investigation of general, reduced to summarize the evidence
of, and objections to, such generally used at present, and
third to investigate the possibilities for the use of Verbalis
in this direction.

Chapter I

OXIDATION-REDUCTION POTENTIALS

For many years it has been conceded that oxidizing and reducing agents of various strengths exist. In the more elementary text-books, we read that Chlorine is a strong oxidizing agent while Hydrogen Peroxide, for example, is a weak one. Some of these books include a list of oxidizing (and reducing) agents in the order of their respective strengths, but until the past few years there was a noticeable lack of similarity in these lists. Books on Analytical Chemistry were even worse as the authors of them either neglected the matter entirely or else passed over it with a few generalities, they, apparently, being unacquainted with the accumulated data of Electro-Chemistry and its possible applications to oxidation-reduction processes.

Blasdale¹² in 1917 inserted a few paragraphs in his text, but it was not until the publication, in Germany, of Muller's¹³ book that any real attempt was made in this direction. In 1924 Popoff¹⁴ brought out the first book in this country which included any adequate discussion of these principles as applied to analytical problems. This was followed by that of Fales¹⁵ in 1925, and the first of the Furman¹⁶ translations of the works

12. W. C. Blasdale, Prin. of Quant. Anal. (1917)
13. E. Muller, Die Eletrometriche Massanalyse. (1923)
14. S. Popoff, Quant. Anal. (1924)
15. H. A. Fales, Inorg. Quant. Anal. (1925)
16. I. M. Kolthoff, Potentiometric Titrations (1926)
Translated by Furman

OXIDATION-REDUCTION POTENTIALS

For many years it has been recognized that oxidation and reduction potentials of various substances exist. In the more elementary text-books, we find that oxidation is a strong oxidizing agent while hydrogen peroxide, for example, is a weak one. Some of these books include a list of oxidation (and reduction) agents in the order of their respective strengths, and until the past few years there was no noticeable lack of reliability in these lists. Books on Analytical Chemistry were even more so the sources of these lists. However, the latter quality of this aspect over its kind is now questioned. They, apparently, have been associated with the accumulation of Electro-Chemistry and the possible application to various reactions processes.

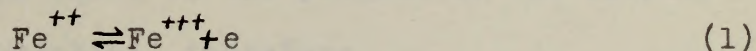
Blaschke¹² in 1927 inserted a few paragraphs in his text, but it was not until the publication, in Germany, of Muller's book that any real attempt was made in this direction. In 1934 Potoff¹³ brought out the first book in this country which included any degree of discussion of these principles as applied to analytical problems. This was followed by that of Valis¹⁴ in 1935, and the first of the Russian¹⁵ translations of the same

12. W. G. Blaschke, *Prin. of Quant. Anal.* (1927)
 13. E. Muller, *Die Elektrochemische Messung* (1933)
 14. S. Potoff, *Quant. Anal.* (1934)
 15. E. A. Valis, *Quant. Anal.* (1935)
 16. E. A. Valis, *Electrochemical Potentials* (1936)
- Translated by Thomas

of Kolthoff in 1926, since which time this material has been included in all of the up-to-date text-books on the subject.

Theory

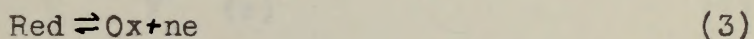
It is universally accepted that the usual rules of equilibrium can be applied to all such oxidation and reduction reactions as are reversible.¹⁷ When we consider that in terms of our modern electrical theory of matter, oxidation is merely a loss of one or more electrons, while reduction is a corresponding gain, we may consistently write, for example, the oxidation of Ferrous ions as follows



and calculate the equilibrium constant to be

$$\frac{(\text{Fe}^{+++})(e)}{(\text{Fe}^{++})} = K \quad (2)$$

or as a general case for the reaction



if we let (Ox) represent the concentration of the substance in its higher state of oxidation, (Red) the concentration of the substance in its lower state of oxidation, n the number of electrons involved, and (e) the so-called "electron concentration", we obtain the general equilibrium constant

$$\frac{(\text{Ox})(e)^n}{(\text{Red})} = K \quad (4)$$

In such reactions as include a change in the Hydrogen ion concentration, this raised to the proper power, must also be included in the numerator.

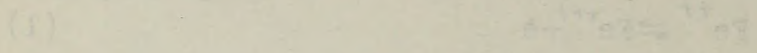
17. H. S. Taylor, Treatise on Phys. Chem., II, 843 (1925)

of Kelland in 1932, since which time this material has been included in all of the up-to-date text-books on the subject.

Theory

It is universally accepted that the usual laws of equilibrium can be applied to all such oxidation and reduction reactions as are reversible. When we consider that in the case of our modern electrical energy in matter, oxidation is not a loss of one or more electrons, while reduction is a corresponding gain, we may conveniently write, for example, the

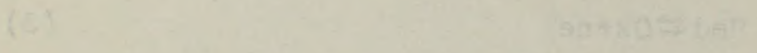
oxidation of potassium ions as follows



and calculate the equilibrium constant for the

(2)
$$\frac{(K^+)(e^-)}{(K)} = K$$

of the constant K for the reaction



If we let (K^+) represent the concentration of the substance in the higher state of oxidation, (K) the concentration of the substance in the lower state of oxidation, n the number of electrons involved, and (e^-) the so-called "electron concentration", we obtain the general equilibrium constant

(4)
$$\frac{(Ox)(e^-)^n}{(Red)} = K$$

In such reactions as involve a change in the electron ion concentration, this factor is the proper constant, and also be included in the numerator.

According to Clark*, an inert electrode contains free electrons and to their concentration we can give a value A, a constant for any electrode system. If this electrode is dipping into a solution of an oxidizing or reducing agent in which the electron concentration has a value (e), the work done W in transferring one faraday from a concentration A to a concentration (e) is

$$W = RT \ln \frac{A}{(e)} \quad (5)$$

where R and T have the values given below.

But this work is also equal to the product of the faraday and the electrode potential, therefore

$$W = EF = RT \ln \frac{A}{(e)} \quad (6)$$

Solving this expression for E, we obtain

$$E = \frac{RT}{F} \ln \frac{A}{(e)} \quad (7)$$

where E= Potential of the electrode(in volts)

R= The gas constant(in joules)

T= The temperature(in degrees Kelvin)

F= 96,500 coulombs(one faraday)

A= A constant(see above)

(e)= The "electron concentration"

ln= Natural logarithm

This equation can be simplified by assuming a temperature of 18 degrees Centigrade and substituting the proper values,

* See reference 10, page

According to O'Brien, an inert electrode contains free electrons and to their concentration we can give a value A , a constant for any electrode system. If the electrode is dipping into a solution of an oxidizing or reducing agent in which the electron concentration has a value (e) , the work done W in transferring one faraday from a concentration A to a concentration (e) is

$$W = RT \ln \frac{A}{(e)} \quad (6)$$

Since E and F have the values given below, but this work is also equal to the product of the faraday and the electrode potential, therefore

$$W = EF = RT \ln \frac{A}{(e)} \quad (7)$$

Solving for expression for E , we obtain

$$E = \frac{RT}{F} \ln \frac{A}{(e)} \quad (8)$$

where E - Potential of the electrode (in volts)

R - The gas constant (in calories)

T - The temperature (in degrees Kelvin)

F - 96,500 coulombs (one faraday)

A - A concentration (arbitrary)

(e) - The "electron concentration"

\ln - Natural logarithm

This equation can be simplified by assuming a temperature of 25 degrees Centigrade and substituting the proper values.

* See reference 10, page 4

and the following form obtained.

$$E = A' - .058 \log(e) \quad (8)$$

Where A' is a constant, log refers to logarithm to the base ten, and the other terms have the same meaning as in (7).

Solving equation (4) for (e) we obtain

$$(e) = \sqrt[n]{\frac{(Red)}{(Ox)}} K \quad (9)$$

Substituting this value for (e) in (8), we obtain

$$E = A' - \frac{.058 \log K}{n} - \frac{.058 \log (Red)}{n (Ox)} \quad (10)$$

and, for the special case where (Red) is equal to (Ox), the third term drops out giving

$$E = A' - \frac{.058 \log K}{n} = E_0 \quad (11)$$

where E_0 is the Normal potential of the system as given in the literature.¹⁸ Substituting this value back in (10) gives

$$E = E_0 - \frac{.058 \log (Red)}{n (Ox)} \quad (12)$$

which is the general form of the equation desired. However, if the reaction includes a change in the Hydrogen ion concentration as below



the equilibrium constant will obviously be

$$\frac{(Ox)(e)^n(H)^m}{(Red)} = K \quad (14)$$

When this is solved for (e), substituted in (8) as above

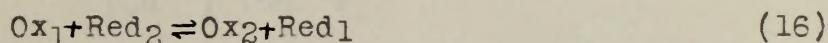
18. R. Gerke, Chem. Rev., 1, 377 (1925)

we obtain

$$E = E_0 - \frac{.058 \log(\text{Red})}{nF} \frac{1}{(\text{Ox})(H^+)^m} \quad (15)$$

Application

During an actual titration we have a reduction of one substance going on at the same time as we have an oxidation of a second substance. This can be written (if n is one)



where Ox_1 is the oxidizing agent and Red_2 the reducing agent.

Applying the usual equilibrium conditions, we obtain

$$\frac{(\text{Ox}_2)(\text{Red}_1)}{(\text{Red}_2)(\text{Ox}_1)} = K \quad (17)$$

and since at the equilibrium point, the two oxidation potentials must be equal

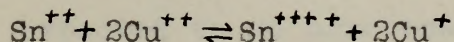
$$E_{01} - \frac{.058 \log(\text{Red}_1)}{(\text{Ox}_1)} = E_{02} - \frac{.058 \log(\text{Red}_2)}{(\text{Ox}_2)} \quad (18)$$

solving this expression we obtain

$$\log K = \frac{E_{01} - E_{02}}{.058} \quad (19)$$

By substituting the values of the Normal Potentials in this equation, we are able to obtain the ratios of the reacting substance at their equivalence point, and from this to predict the extent to which the reaction has gone. Two illustrations will probably show this a little more clearly.

First considering the reaction between Stannous ions and Cupric ions to give Stannic ions and Cuprous ions.



In this case, n is two $2(E_{O_1} - E_{O_2})$

$$\log K = \frac{\quad}{.058}$$

$$\log K = \frac{2(.138 - .18)}{.058}$$

$$K = .722$$

$$\frac{(Cu^+)^2 (Sn^{+++})}{(Cu^{++})^2 (Sn^{++})} = K$$

but at the equivalence point

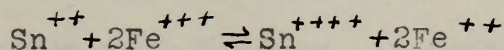
$$\frac{(Sn^{+++})}{(2Cu^+)} = \frac{(Sn^{++})}{(2Cu^{++})} \text{ or } \frac{(Cu^+)}{(Cu^{++})} = \frac{(Sn^{+++})}{(Sn^{++})}$$

therefore substituting in the above equation

$$\frac{(Cu^+)}{(Cu^{++})} = \sqrt[3]{K} = .896$$

or the reduction of the Cupric ions could not be quantitatively accomplished by the Stannous ions.

But, by applying the same line of reasoning to the reaction between Stannous ions and Ferric ions,



we find that

$$\log K = \frac{2(.138 - .714)}{.058}$$

$$K = 3 \times 10^{20}$$

and

$$\frac{(Fe^{++})}{(Fe^{+++})} = \sqrt[3]{K} = 6.7 \times 10^6$$

or as far as can be calculated from this principle, this reaction can be expected to go practically to completion.

In this case, $n = 1.5$

$$\log K = \frac{1}{n} \log \frac{1}{1 - \frac{1}{n}}$$

$$\log K = \frac{1}{1.5} \log \frac{1}{1 - \frac{1}{1.5}}$$

$$K = 1.732$$

$$\frac{(1.732)^{1.5}}{(1.732)^{1.5}} = 1$$

but the resistance point

$$\frac{(1.732)^{1.5}}{(1.732)^{1.5}} = \frac{(1.732)^{1.5}}{(1.732)^{1.5}}$$

therefore substitution in the above equation

$$\log K = \frac{1}{n} \log \frac{1}{1 - \frac{1}{n}}$$

of the resistance of the circuit can be calculated

according to the following table.

But, in applying the above formula of resistance to the

resistor between standard and ratio

$$R = \frac{1}{K} = \frac{1}{1.732} = 0.577$$

we find that

$$\log K = \frac{1}{n} \log \frac{1}{1 - \frac{1}{n}}$$

$$K = 1.732$$

and

$$\frac{(1.732)^{1.5}}{(1.732)^{1.5}} = \frac{(1.732)^{1.5}}{(1.732)^{1.5}}$$

or we can calculate from the following table

the value of the resistance to be calculated

While from these considerations, we can predict that a reduction or an oxidation will proceed quantitatively in the reverse case "one should never fail to test the theoretical deductions experimentally, and should not be content merely with the result of the computations!"¹⁹

Measurement

Every titration cell contains two electrodes and the solution which is being titrated. The measured voltage of the cell is the algebraic difference of the actual potential differences between the two electrodes and the solution. One of these electrodes is known as the indicator electrode, since it acts as an indicator for the substance, or substances the potential of which it is desired to measure; the other is known as the reference electrode since its potential is constant. In this particular case the tenth-normal Calomel electrode was used as the reference electrode. This consists of a layer of Mercury, covered by a paste of Mercurous Chloride intimately mixed with Mercury, in contact with a solution of Potassium Chloride, containing 7.455g. in a liter of distilled water which has been previously saturated with Mercurous Chloride.(Fig. 1) This electrode has a potential of 0.609 volts referred to the Normal Hydrogen electrode. The indicator electrode used was merely a short piece of bright Platinum wire which had been fused into the end of a piece of glass tubing.(Fig. 2)

19. I. M. Kolthoff, Volumetric Analysis, I, 115 (1928)

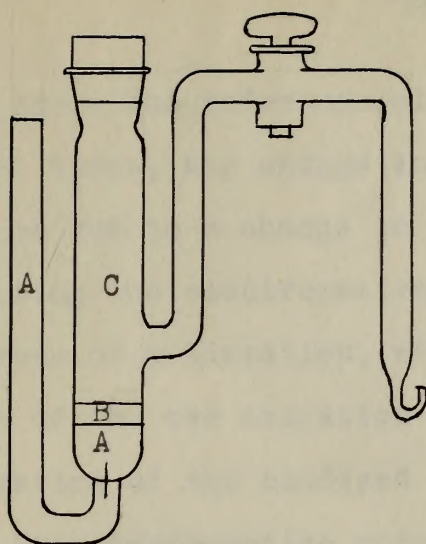


Figure 1

Calomel Electrode

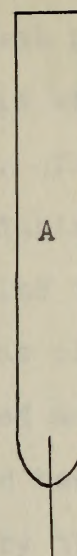


Figure 2

Platinum Electrode

- A Mercury
- B Mercury-Calomel Paste
- C Tenth Normal Potassium Chloride Solution

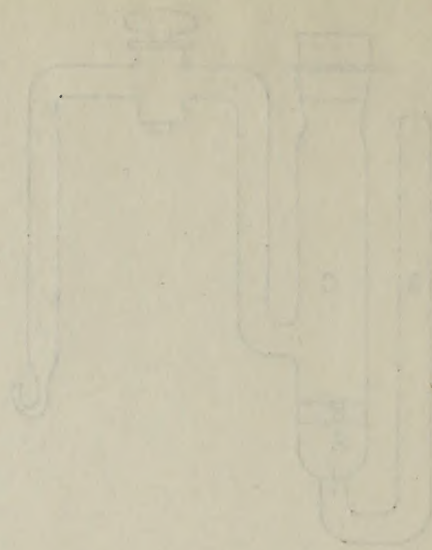


Figure 1
Chloro-Formate

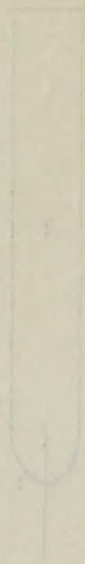


Figure 2
Plasma Nitrate

A. Mercury
B. Mercury-Formate
C. Fresh-Formate
D. Chloro-Formate

Since the reference electrode has a constant potential at all times, any change in the measured voltage of the cell must be due to a change in the solution itself. Thus by measuring the electromotive force of the cell during the progress of a titration, we are able to determine the variation of the two oxidation potentials due to the change in the ratios of the oxidized states to the reduced states.

The electromotive force of such a cell can best be measured by the use of a potentiometer, since by the use of a voltmeter, too much current would be drawn from the cell and electrolysis would result. The principle of the potentiometer can be explained as follows. If a source of electromotive force be connected to the ends of a wire AB, of uniform resistance, the drop in potential along the wire will be uniform also. If now a second source of electromotive force, weaker than the first, be connected to A and through a galvanometer to a slider on this wire in such a way that they are opposing each other, and this slider is moved to some point C, so that no deflection is shown by the galvanometer, the voltage of the first source will be to the voltage of the second source as AB/AC , since the potential drop between A and C is proportional to the length.

For practical purposes it is preferred to first balance the potentiometer using a standard cell against one of unknown but constant value, and then substitute the cell which it is desired to measure in place of the standard cell. This can

Since the potential difference has a constant potential
at all times, any change in the potential difference of the cell
must be due to a change in the resistance itself. Thus by
measuring the electromotive force of the cell during the
operation of a circuit, we are able to determine the vari-
ation of the two galvanic potentials due to the change in
the forces of the oxidized species in the reduced states.
The electromotive force of such a cell can best be
measured by the use of a potentiometer, since by the use of
a voltmeter, the small current would be drawn from the cell
and electromotive force would be affected. The principle of the poten-
tiometer can be explained as follows. If a source of electro-
motive force is connected to the ends of a wire AB, of uni-
form resistance, the drop in potential along the wire will
be uniform also. If now a second source of electromotive
force, weaker than the first, be connected to a wire AC, of uni-
form resistance, the drop in potential along the wire will
be given by the ratio of the length of the wire to the length of
the wire. If the two wires are connected at a point C, the
potential difference between the ends of the wire AC will be the same
as the potential difference between the ends of the wire AB. If
the voltage of the first source will be E_1 and the voltage
of the second source is E_2 , since the potential drop be-
tween A and C is proportional to the length
of the wire, we have $E_1 \propto AC$ and $E_2 \propto BC$. For practical purposes it is preferred to have the
potentiometer using a standard cell against one of unknown
but constant value, and then substitute the cell whose value is to
be determined in place of the standard cell. This can

be better understood by reference to the following diagram,²⁰ which shows the complete circuit including the potentiometer, battery, standard cell, galvanometer, switch, keys, and protective resistance, the electrodes of the cell being connected to the positions marked E.M.F.

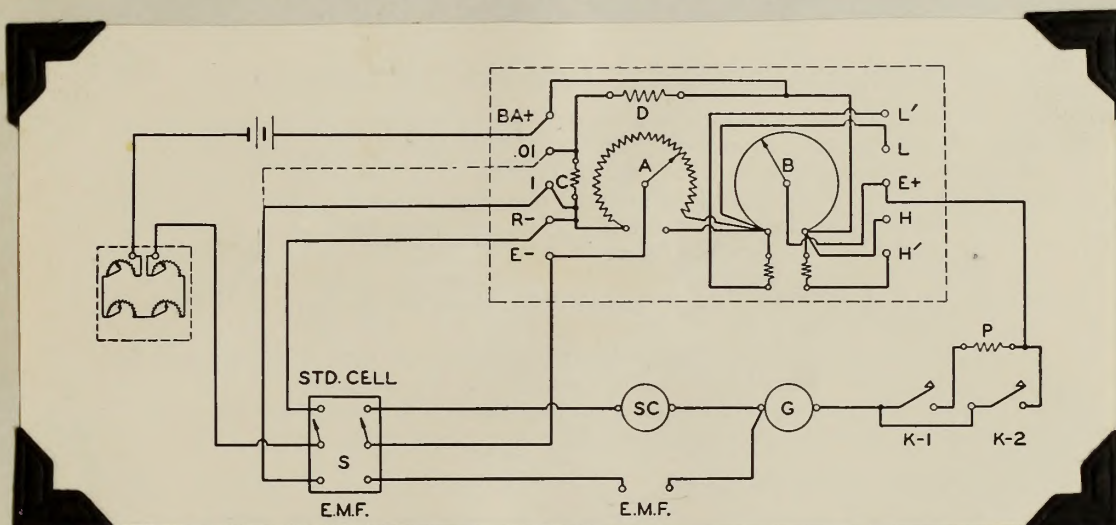


Fig. 3

The potentiometer is first standardized against the standard cell SC by throwing it in by means of the switch S, and putting sufficient resistance in the battery circuit to give no deflection in the galvanometer G when the key K-2 is tapped, provided that the potentiometer contacts A and B have been first set to read the voltage of the standard cell. The switch S is then thrown in the opposite direction so as to put the unknown cell in circuit, the contacts A and B are then moved until the circuit is again balanced as shown by

20. Leeds and Northrup, Bulletin #765 (1926)

be better understood by reference to the following diagram,
which shows the general circuit including the potentiometer,
battery, standard cell, galvanometer, switch, lamp, and
protective resistance, the elements of the cell being
connected to the potentiometer, which is connected to the
galvanometer, which is connected to the standard cell, which
is connected to the battery, which is connected to the lamp.

APPLICATIONS OF THE POTENTIOMETER

The potentiometer is used to measure the electromotive force of a cell, or the potential difference between two points in a circuit. It is also used to compare the electromotive forces of two cells, or to determine the internal resistance of a cell. The potentiometer is a device which consists of a long wire of uniform cross-section, and a sliding contact which can be moved along the wire. The wire is connected to a battery, and the sliding contact is connected to a galvanometer. The electromotive force of the cell to be measured is connected to the sliding contact, and the galvanometer is used to measure the current flowing through the wire. The position of the sliding contact is adjusted until the galvanometer shows zero deflection, and the length of the wire between the battery and the sliding contact is measured. This length is proportional to the electromotive force of the cell.

Fig. 1

The potentiometer is first standardized by connecting the standard cell to the sliding contact, and adjusting the position of the sliding contact until the galvanometer shows zero deflection. This is done by moving the sliding contact along the wire until the galvanometer shows zero deflection. The length of the wire between the battery and the sliding contact is then measured, and this length is used as a standard for measuring the electromotive force of other cells. To measure the electromotive force of a cell, the cell is connected to the sliding contact, and the position of the sliding contact is adjusted until the galvanometer shows zero deflection. The length of the wire between the battery and the sliding contact is then measured, and this length is compared with the standard length to determine the electromotive force of the cell. The potentiometer is also used to compare the electromotive forces of two cells, by connecting the two cells to the sliding contact, and adjusting the position of the sliding contact until the galvanometer shows zero deflection. The lengths of the wire between the battery and the sliding contact for the two cells are then measured, and these lengths are compared to determine the ratio of the electromotive forces of the two cells. The potentiometer is also used to determine the internal resistance of a cell, by connecting the cell to the sliding contact, and adjusting the position of the sliding contact until the galvanometer shows zero deflection. The length of the wire between the battery and the sliding contact is then measured, and this length is compared with the standard length to determine the internal resistance of the cell.

no deflection in the galvanometer G when key K-2 is tapped, and the reading of the positions of A and B is the voltage of the unknown cell. The key K-1 is in series with the protective resistance P and is used in obtaining an approximate balance, before using the other key.

The apparatus used in this investigation was as follows

Leeds and Northrup Student's Potentiometer

Leeds and Northrup 4-Dial Resistance Box

Leeds and Northrup Portable Pointer Galvanometer

Eppley Standard Cell, 1.01880 Volts

The electrodes described previously, D. P. D. T. Switch, tapping keys, protective resistance, and two dry cells.

no deflection in the galvanometer 3 when key K-2 is tapped, and the reading of the positions of A and B is the voltage of the unknown cell. The key K-1 is to serve with the protective resistance R and is used in connecting an external source balance, before using the other key.

The apparatus used in this investigation was as follows:
Leads and Wottrup Standard's Potentiometer
Leads and Wottrup 4-Unit Resistance Box
Leads and Wottrup Potentiometer Galvanometer
Epstein Standard Cell, 1.01830 Volt
The electrodes described previously, C. E. F. Series, tapping keys, protective resistance, and two dry cells.

Chapter II

THE COMMON REDUCING AGENTS

Ferrous Salts

The first reducing solution usually prepared in elementary quantitative analysis is a Ferrous salt, either the simple Sulfate or the double Ammonium Sulfate. The reason for this primacy can not be due to its importance since a review of the literature of Analytical Chemistry shows only four methods, all indirect, which are of any importance. The method of Blair²¹ for Chromium in which the ore is oxidized by means of Sodium Peroxide to a Chromate, acidified, treated with a measured volume of the standard Ferrous solution, and the excess determined by titrating with standard Potassium Dichromate, is generally considered the standard method for that element. Treadwell,²² however, prefers to perform this analysis iodometrically. Lunge's²³ method for the estimation of Manganese Dioxide in which the sample is treated with an excess of Ferrous salt in Sulfuric Acid, and the excess determined by the titration with Potassium Permanganate, has been replaced by the method of Fresenius and Mohr²⁴ in which Oxalate is substituted for the Ferrous salt in spite of the possible dehydrating effect of Sulfuric Acid.

In certain steel works laboratories, Manganese in the

21. A. H. Low, Tech. Meth. of Ore Anal. 9th Ed. 74 (1922)
22. F. H. Treadwell, Quant. Anal. 4th Ed., 675 (1915)
23. G. Lunge, Chem.-Techn. Untersuchungsmethodik, 6th Ed., 569 (1913)
24. A. H. Low, Tech. Meth. of Ore Anal. 9th Ed., 142 (1922)

Chapter II

THE COMMON REDUCING AGENTS

Various Agents

The first reducing substance usually prepared is the
mercuric chloride. This is a white solid, which is
easily soluble in the acids. The reason
for this property can not be due to the fact that since a
review of the literature of Analytical Chemistry shows only
few methods, all indirect, which are of any importance.
The method of Blair¹ for the estimation of iron is the only one
by means of ferrous chloride to a carbonate, which is, treated
with a measured volume of the standard ferrous solution, and
the excess determined by titration with standard potassium
dichromate, is generally considered the standard method for
this element. Truesdell,² however, prefers to perform this
analysis iodometrically. Lund's³ method for the estimation
of manganese dioxide in which the sample is treated with an
excess of ferrous salt in sulfuric acid, and the excess de-
termined by the titration with potassium permanganate, has
been replaced by the method of Truesdell and Lund⁴ in which
dioxide is substituted for the ferrous salt in acid of the
possible oxidative effect of sulfuric acid.

In certain cases where laboratory, manganese is
1. A. N. Low, Tech. Meth. of Ore Anal., Vol. IV (1925)
2. F. H. Truesdell, Chem. Anal., Vol. IV (1925)
3. G. Lund, Chem.-Tech. Untersuchungs-Zeit., 52, 55
4. F. H. Truesdell and G. Lund, Tech. Meth. of Ore Anal., Vol. IV (1925)

steel(or iron) is determined by oxidizing it, using either the Bismuthate or the Persulfate method and reducing the resulting Permanganic acid with Ferrous²⁵ salt. As this procedure is now included in Method of Testing A-33-24 (when Chromium is absent) of the American Society of Testing Materials, it may be considered as of some importance.

The fourth use of a Ferrous solution is for the determination of Vanadium in Ferro-Vanadium by the standard method of the American Vanadium Co.²⁶ In this method, after both the Iron and Vanadium have been oxidized by Permanganate, an excess of a Ferrous solution is added, and the latter determined with standard Bichromate solution.

Treadwell also mentions the method of LeBlanc and Eckhardt²⁷ for the determination of Persulfates by the use of Ferrous solution while Scott seems to prefer this to Oxalic Acid method of Kempf²⁸

Possibly this lack of procedures involving the use of Ferrous salts is largely influenced by their lack of stability. While it is generally considered that Ferrous salts are unstable, practically no work has been done in order to ascertain the conditions necessary for maximum stability.

- 25. S. Popoff, Quant. Anal., 2nd Ed., 499 (1927)
- 26. W. W. Scott, Stan. Meth., 4th Ed., 142 (1922)
- 27. LeBlanc and Eckhardt, Chem. News, 81, 38 (1900)
- 28. R. Kempf, Ber., 38, 3963 (1905)

... (or iron) is determined by oxidizing it, using silver
the elements of the ferrous salt and reducing the
resulting ferrous salt with ferrous ... in this
... it is now included in the ... A-33-34
(when ... is absent) of the ... of ...
... it may be considered as a ...
The fourth use of a ferrous solution is for the deter-
mination of ... in ... by the ...
of the to this ...
... have been ...
... of a ferrous solution is added, and the ...
... with ...
... also mentions the use of ...
... for the determination of ... by the use of
... with ... to ...
... of ...
... the use of
... is largely influenced by their lack of ...
... it is especially ...
... no work has been done in other ...
... for maximum ...

- 22. E. ... (1932)
- 23. W. ... (1932)
- 24. ... (1932)
- 25. ... (1932)
- 26. ... (1932)

Oxalic Acid and Oxalates

In 1882, Zimmerman²⁹ investigated the reactions between Permanganate and Oxalic Acid in both Hydrochloric and Sulfuric acid solution and came to the conclusion that the reaction took place quantitatively above 70 degrees centigrade. During the next twenty years, a few chemists used Oxalic Acid as a reducing agent, but it was not until about 1903 when Sorenson³⁰ finished his researches on the Sodium salt that bears his name that it replaced Iron wire as the common means of standardizing Permanganate solutions. As a result of this reaction Oxalic Acid or acidified Oxalate is commonly used in many cases of indirect analysis of oxidizing agents, the excess being titrated with Permanganate.

Among these are the Fresenius-Mohr* method for Manganese Dioxide mentioned previously and the similar methods of Lux³¹ for Lead Dioxide and red lead. In the presence of a Manganese Salt and Nitrate, Nitric Acid reacts with Oxalic Acid³² quantitatively, and Debourdeaux³³ similarly used Oxalic Acid to determine Chlorates, Bromates and Iodates. Kempf worked out the method for the analysis of Persulfates** by means of Oxalic Acid in the presence of Silver Sulfate as a catalyst mentioned previously.

29. Zimmerman, Ann. 213,305 (1882)

30. S. P. L. Sorenson, Z. anal. Chem. 42,513 (1903)

*. See Ref. page 15

31. Lux, Z. Anal. Chem, 19,153 (1880)

32. I. M. Kolthoff, Vol. Anal. II, 338 (1929)

33. Debourdeaux, Compt. rend., 136, 1668 (1903)

**. See Ref. 28, page 16

Crystalline Acid and Oxidation

In 1933, Elmer²⁶ investigated the reaction between

Permanganate and Oxalic Acid in both hydrochloric and

sulfuric acid solutions and came to the conclusion that the

reaction took place quantitatively above 10 normal permang-

enate. During the next twenty years, a few chemists over-

Crystalline Acid as a reducing agent, but it was not until about

1905 when Sommers²⁷ claimed the importance of the reaction

and that permanganate was used in the reaction from which the

excess amount of permanganate was determined. As a

result of this reaction Oxalic Acid or potassium oxalate is

commonly used in many cases of indirect analysis of oxidizing

agents, the excess being titrated with Permanganate.

Among others are the Thiochrome-Hoff²⁸ method of determining

Chlorine combined with organic and inorganic substances of low²⁹

for both Thiochrome and red light. In the presence of a substance

with and without, Nitric Acid reacts with Oxalic Acid³⁰

quantitatively, and Sommers²⁷ and others have used Oxalic Acid

to determine Chlorine, Bromine and Iodine. Kohn³¹ states

that the method for the analysis of Permanganate is based on

Oxalic Acid in the presence of Silver Nitrate as a catalyst

mentioned previously.

26. Elmer, *Anal. Chem.* 12, 305 (1933).
27. S. F. Sommers, *J. Anal. Chem.* 44, 44 (1925).
28. Thiochrome-Hoff, *Anal. Chem.* 10, 100 (1920).
29. Kohn, *J. Anal. Chem.* 10, 100 (1920).
30. I. M. Kohn, *Anal. Chem.* 11, 335 (1921).
31. Sommers, *Anal. Chem.* 12, 305 (1933).

In passing two other methods involving the reducing action of Oxalic Acid should be mentioned. One of these that of Luckow³⁴ in which Calcium (from a soluble salt) is precipitated as Oxalate, and Oxalate subsequently titrated is very satisfactory. The second, that of Kolthoff³⁵ for organic substances in which the substances are oxidized to Oxalate in alkaline solution which in turn is oxidized with Permanganate, is as yet of limited usefulness.

The stability of Oxalic Acid solutions has been investigated as long ago as 1898 by Jorissen³⁶ who found that it was slowly oxidized to water and Carbon Dioxide when exposed to the light. Later it was found that it also decomposed somewhat with the formation of Carbon Monoxide as well. Kolthoff,³⁷ however, found that a tenth normal solution did not change even after a year if kept in the dark.

Arsenious Acid

Arsenious Acid has been in use as a reducing agent at least since 1852, when Penot³⁸ published his method for the determination of Hypochlorites. This is the well-known method used to evaluate the "available Chlorine" of bleaching powder in which the active material is extracted with water and an aliquot portion is titrated with standard Arsenious Acid until a drop of the solution does not turn Potassium

34. Luckow, Z. anal. Chem., 26, 9 (1887)

35. I. M. Kolthoff, Vol. Anal. II, 339 (1929)

36. W. P. Jorissen and H. F. Izn, Z. anal. Chem., 23, 726 (1910)

37. I. M. Kolthoff, Vol. Anal. I, 239 (1928)

38. Penot, Bull. Soc. Ind. de Mulhouse, 118 (1852)

Iodide starch paper blue. Scott³⁹ gives an improved method in which Potassium Iodide is added and the liberated Iodine titrated directly.

Arsenious Acid in a Sodium Bicarbonate solution is frequently used to standardize Iodine⁴⁰ solution, and, according, to Gyory⁴¹ in Hydrochloric Acid solution to standardize Bromate solutions. Pyrolusite and certain Peroxides which can liberate Iodine by Bunsen's distillation method⁴² can also be determined much better with Arsenious Acid according to Lunge-Berl⁴³ than by the use of the usual Thiosulfate. Feit⁴⁴ makes use of the ability of Arsenious Acid in alkaline solution to reduce Mercuric salts to metallic Mercury as a means of analyzing such salts, but apparently other methods are preferred. Since Arsenious Acid is not affected by Persulfate it has become the preferred solution in the determination of Manganese in steel by the Persulfate⁴⁵ method and is frequently substituted on account of its greater stability for a Ferrous Salt in the Bismuthate⁴⁶ method for that element.

It is probable that many other uses might be found for this reducing agent, but since we can in most cases get as satisfactory results with Sodium Thiosulfate, one which

39. W. W. Scott, Stand. Meth. of Chem. Anal., 155 (1927)
40. S. Popoff, Quant. Anal. 2nd Ed., 156 (1927)
41. G. Gyory, Z. anal. Chem., 32, 415 (1893)
42. F. B. Treadwell, Quant. Anal. 4th Ed., 661 (1915)
43. G. Lunge-Berl, Chemisch-Technische Untermethoden 7th Ed., 972 (1921)
44. W. Feit, Z. anal. Chem., 28, 318 (1889)
45. G. v. Knorre, Z. angew. Chem., 14, 1149 (1901)
46. H. A. Fales, Inorganic Quant. Anal., 338 (1925)

directly or indirectly covers a much broader field, little progress will probably be made in that direction in the immediate future.

Titanous salts

The availability of Titanous salts was suggested by Ebelman⁴⁷ in 1847, who showed that they were capable of reducing quantitatively the salts of Copper and Iron. In 1876, Glatzel⁴⁸ published an article on this subject, but it was not until 1903, when Knecht⁴⁹ started his intensive investigations on these solutions that any serious attention was paid to them. Anyone reading the well-known monograph of Knecht and Hibbert⁵⁰ might well imagine that here we have the ideal and universal reducing agent. According to this book, a Titanous solution will react quantitatively with the salts of Iron and Copper, Chromium, Tin, Tungsten, Molybdenum, Vanadium, Lead, Manganese, Cobalt, in addition to Hydrogen Peroxide, Chlorates, Perchlorates, Persulfates, Nitrates, Hydrosulfates and Sulfates, numerous types of organic compounds, including many common dyestuffs, and can even be used to determine the degree of mercerization of cotton.

In spite of these claims Titanous salts are rarely used in most analytical laboratories. Treadwell lists only three methods involving the use of Titanous Chloride, the method of

47. Ebelman, Ann. chim. phys., 20, 385 (1847)

48. E. Glatzel, Ber., 9, 1829 (1876)

49. E. Knecht, Ber., 33, 1550 (1903)

50. E. Knecht and E. Hibbert, New Red. Meth. in Vol. Anal. 2nd Ed., (1925)

directly or indirectly covers a much broader field, it is

probable that it will be made in that direction in the

near future.

There are also

The availability of titanium salts was suggested by

Stewart¹ in 1947, who showed that they were capable of

reducing quantitatively the salts of copper and iron. In

1950, Glatzel² published an article on this subject, but it

was not until 1953, when Knecht³ started his investigations in-

vestigations on these reactions that any serious attention

was paid to them. Knecht's results for well-known compounds

of lead and silver⁴ might well lead to the idea that we have

the ideal and universal reagent as yet. According to this

idea, a titanium reagent will reduce quantitatively all the

salts of iron and copper, cobalt, nickel, vanadium, molybdenum,

vanadium, lead, tungsten, cobalt, in addition to hydrogen

peroxide, chlorate, perchlorate, persulfate, nitrate,

hypochlorite and sulfate, numerous types of organic compounds,

including many common dyes, and can even be used to

determine the degree of reduction of oxides.

In spite of these claims titanium salts are rarely used

in most analytical laboratories. This is due to the fact

that methods involving the use of titanium dioxide, the method of

1. Stewart, J. Am. Chem. Soc., 69, 282 (1947).
2. Glatzel, Ber., 83, 1532 (1950).
3. Knecht, Ber., 86, 1532 (1953).
4. Knecht and E. Knecht, Ber., 86, 1532 (1953).
5. Knecht and E. Knecht, Ber., 86, 1532 (1953).

Knecht and Hibbert for Ferric Iron in which a direct titration is made using a Thiocyanate indicator, the same authors' method for the determination of Hydrogen Peroxide, a direct titration, and their indirect method for the determination of Persulfates using a Ferric salt. Scott gives only the modification of Thornton and Chapman⁵¹ for the iron determination and mentions no other use. Kolthoff also includes this method and adds the various methods for determining Cupric Copper and recommends a new procedure for the analysis of organic nitro compounds.⁵²

Probably the chief reason for the failure of Titanous salts to be used more generally is due to their lack of stability. When exposed to the air both the Chloride and Sulfate take up oxygen and rapidly lose their reducing strength. There is also a photo-chemical reduction in which the Titantic salt and Hydrogen is formed. In order to overcome the first of these difficulties a particular form of apparatus must be used in conjunction with the burette so that the solution is at all times exposed to an atmosphere of hydrogen. The second can be somewhat overcome by not exposing the solution to sunlight, but even with these precautions the solution must be frequently standardized.

Sodium Thiosulfate

As before mentioned,^{*} Sodium Thiosulfate has been in constant use as a reducing agent practically since the beginning

51. E. Knecht and E. Hibbert, New Reduction Meth. in Vol. Anal. 2nd Ed., (1925)

52. I. M. Kolthoff and C. Robinson, Rec. Trav. Chim., 46, 169 (1926)

*. See Ref. 9 page

...and Hibbert for their work in which a direct relation
is made between the Thomsen reaction and the heat of solution
for the determination of hydrogen peroxide, a direct relation
and their indirect method for the determination of peroxide

...which a direct relation is made between the Thomsen reaction
and the heat of solution for the determination of hydrogen peroxide
no other use. Kohnstamm also indicates this method and notes the
various methods for determining hydrogen peroxide and recommends a
new procedure for the analysis of organic hydrogen peroxide.

Probably the chief reason for the failure of this
method to be used more generally is due to the fact that the
hydrogen peroxide is not stable in the air and the solution is not
stable up to 100°C and rapidly loses its reducing strength.

There is also a small chemical reaction in which the hydrogen
peroxide is formed. In order to overcome this the first
of these difficulties is a part of the work of Kohnstamm and
used in connection with the method of the analysis is
of this kind exposed to an atmosphere of hydrogen. The reason
one of the most serious is not explained the solution to this
light, but even with these precautions the solution must be

...readily standardized.

Sodium tetraborate

As before mentioned, sodium tetraborate has been used
as a reducing agent particularly since the following

1. E. Kohnstamm and E. Hibbert, *Ann. Chem.*, 1923, 193, 193.
2. I. M. Kohnstamm and C. Robinson, *Ann. Chem.*, 1923, 193, 193.
3. I. M. Kohnstamm and C. Robinson, *Ann. Chem.*, 1923, 193, 193.
4. I. M. Kohnstamm and C. Robinson, *Ann. Chem.*, 1923, 193, 193.

of modern Volumetric analysis. At present it is probably our most valuable substance for that purpose since the reaction between it and Iodine is one of the most accurate of all titrations, and the necessary Iodine can be liberated when a soluble Iodide is treated with practically any substance possessing oxidizing properties. There is, of course, a slight titration error introduced by the use of the Starch indicator, but according to Kolthoff⁵³ at ordinary temperatures it does not amount to more than one half of a cubic centimeter of one thousandth normal solution under the usual conditions of Iodide in concentration, temperature and volume. Due to the reaction between Alkalies and Iodine and other interfering reaction, the pH of the solution should be less than 7.6 for a solution which is tenth normal in Iodine and still less for more dilute solutions.

The method for the determination of Iodine involves nothing more than dissolving it in a strong Iodide solution diluting and titrating directly with standard Thiosulfate adding the Starch when only a small amount of the Iodine remains. If a solution of an Iodate in the presence of excess of Iodide is acidified free Iodine is quantitatively formed which can then be determined as in the preceding case.

Kjeldahl⁵⁴ made use of this same reaction as a means of determining acid in his original method for Nitrogen, but altho Groger,⁵⁵

53. I. M. Kolthoff, Vol. Anal. II, 351 (1929)

54. J. Kjeldahl, Z. anal. Chem., 22, 366 (1883)

55. M. Groger, Z. angew. Chem., 3, 353 (1890)

of organic Voluntary analysis. At present it is probably not
so a voluntary response for that happens since the reaction
between it and iodine in one of the most accurate of all
methods, and the necessary iodine can be liberated when a
soluble iodide is treated with potassium iodide.
Possessing oxidizing properties. There is, of course, a slight
reaction error introduced by the use of the starch indicator,
but according to Volhard²⁵ as ordinary temperatures it does
not seem to interfere with one half of a cubic centimeter of one
decimolar solution under the usual conditions of
iodine in concentration, temperature and volume. Due to the
reaction between alkalies and iodine and other interfering
reaction, the use of the solution should be less than 0.5 for
a solution which is being normal in iodine and still less for
very dilute solutions.

The method for the determination of iodine involves
adding more than 10% of a strong iodine solution
to the sample and reacting directly with standard thiosulfate
adding the starch when only a small amount of iodine
remains. It is a solution of an iodine in the presence of starch
of iodine is soluble. Free iodine is quantitatively formed
which can then be determined as in the preceding case.
Kjeldahl²⁶ and one of his same reaction a method of determining
acid in his original method for nitrogen, but also for²⁷

25. J. H. Volhard, Vol. Anal., 11, 381 (1882).
26. J. Kjeldahl, Z. anal. Chem., 23, 368 (1884).
27. J. Kjeldahl, Z. anal. Chem., 23, 363 (1884).

Schwarz,⁵⁶ Moody⁵⁷ and many others have studied this reaction this method has not displaced the usual basic titration.

Chlorine, Bromine, Dichromates, Permanganates, Ferri-Cyanides, Chlorates, Bromates, Hydrogen, Peroxides, Periodates, Persulfates, Pentavalent Arsenic and Antimony, Vanadate, Ferric Iron, Cupric Copper, Cobalt, Cerium, and Molybdic Acid can be determined by treatment with an excess of Potassium Iodide and the subsequent titration of the Iodine with Thiosulfate. Pyrolusite, Lead Dioxide, Telluric Acid, and similar substances can be determined by treatment with Hydrochloric Acid, catching the liberated Chlorine in an Iodide solution, followed by the usual titration.

During the last thirty years, many attempts have been made to develop analytical methods for the analysis of various organic compounds. Among the most important of these are two which involve the use of Thiosulfate. The first of these, the determination of the "Iodine Number" a measuring of the unsaturation of an oil or fat, consists of allowing a solution of Iodine Chloride,⁵⁸ or Iodine Bromide⁵⁹ to react with the substance adding Potassium Iodide and the usual titration with Thiosulfate. A blank run at the same time and in the same manner furnishes a means of calculating the amount of Halogen absorbed. The other method of Kopperschaar⁶⁰ for Phenol,

- 56. H. Schwarz, Monatsh., 19, 139 (1898)
- 57. S. E. Moody, Z. anorg. Chem., 46, 423 (1905)
- 58. J. J. A. Wijs, Z. anal. Chem., 37, 277 (1898)
- 59. J. Hanus, Z. Untersuch. Nah., 913 (1901)
- 60. W. Kopperschaar, Z. anal. Chem., 15, 233 (1876)

consists in treating the Phenol with Potassium Bromate and Bromide, acidifying and titrating the excess Bromine by adding Iodide and Thiosulfate.

Sodium Thiosulfate solutions as ordinarily prepared are made from boiled water⁶¹ and allowed to stand for several days before standardizing as otherwise the solution is not sufficiently stable, but gains in strength. It has generally been thought that since the boiling of the water removed Carbon Dioxide, it was the resulting formation of Thiosulfurous Acid followed by its breakdown into Sulfurous Acid and free Sulfur that caused this change. This idea is also strengthened by the fact that if a small amount of Sodium Carbonate or Hydroxide is added the stability is greatly increased. Recently Mayr⁶² has found that this change is partly due to the presence of so-called Thio-bacteria, which have the ability to decompose Thiosulfates, but he could not find a substance capable of hindering their action.

61. S. Popoff, Quant. Anal. 2nd Ed., 161 (1927)

62. Mayr, Z. anal. Chem., 68, 274 (1926)

contribute in increasing the amount of the potassium bromide and
sulfate, and also in increasing the amount of the potassium
bromide and sulfate.

Sodium thiosulfate solutions are ordinarily prepared by

adding to a solution of sodium sulfite and allowed to stand for several

days before the addition of the potassium bromide and sulfate.

It is generally stated, but again in question. It is generally

stated that since the boiling of the water treated

with sodium thiosulfate, it is the resulting formation of the sodium

sulfate followed by its conversion into sodium sulfite and then

sulfur that causes this change. This idea is also supported

by the fact that if a small amount of sodium carbonate or

sulfate is added the stability is greatly increased. Recently

Wray¹ has found that this change is partly due to the presence

of so-called thio-bacteria, which have the ability to decompose

thiosulfate, but he could not find a substance capable of

inhibiting their action.

1. Wray, J. and J. E. Smith, J. Biol. Chem., 1917, 31, 103.
2. Wray, J. and J. E. Smith, J. Biol. Chem., 1917, 31, 103.

Chapter III

STANNOUS SALTS as REDUCING AGENTS

Practically the only Stannous salt which has been used as a reducing agent is the Chloride, if we may except those cases where the Sulfate is formed in solution as the result of the addition of Sulfuric Acid. Each of the suggested methods for the use of Stannous Chloride in Volumetric Analysis will be taken up and its desirability considered in each case. In a later chapter, the possibilities for the use of the Perchlorate in those cases where it might be of value will be considered.

The best known method involving the use of Stannous Chloride is the Zimmermann-Reinhardt⁶³ for the determination of Iron. In this method, Ferric Chloride is reduced with Stannous Chloride, while hot, using the color change as the equivalence point, cooling, diluting, removing the excess with Mercuric Chloride, and finally titrating the reduced Iron with standard Potassium Permanganate or Potassium Bichromate. This method is of great importance and is in constant use wherever this element is determined. Its chief source of difficulty seems to be the recognition of the color change when the correct amount of Stannous Chloride has been added. If too much is added, there will be a precipitation of Mercury in the next step, which completely ruins the analysis. It has been

63. Cl. Zimmermann and C. Reinhardt, Chem. Ztg., 13, 160 (1884)

STANNOUS SALTS OF HYDROLYZING AGENTS

Theoretically the only stannous salt which has been given as a reducing agent in the literature, it is very likely that these agents when the sulfate is formed in solution as the result of the addition of sulfuric acid. Each of the elements between the use of stannous chloride is known to be reduced in the presence of an acid and its hydrolysis is indicated in each case. In a later chapter, the possibilities for the use of the stannous salt in the reduction of organic compounds will be considered.

The best method for the reduction of stannous chloride is the stannous chloride method for the determination of iron. In this method, ferric chloride is reduced with stannous chloride, while not, using the color change as the evidence of the reduction, allowing the color to change from brown to colorless, and finally obtaining the colorless iron with stannous chloride. This method is of great importance and is in constant use wherever this element is determined. The color change of stannous chloride is the result of the reduction of the color change from the colorless stannous chloride to the colorless stannous chloride. It is known that when there will be a precipitation of stannous chloride in the solution, which will cause the analysis. It has been

claimed that the precipitated Mercurous Chloride reduces the Ferric Chloride⁶⁴ formed in the titration, but, if only a slight excess of Stannous Chloride was added, this effect is so small as to be negligible. This method differs from those which follow as in it the Stannous Chloride is not used as a titrating solution.

Fresenius,⁶⁵ in 1886, took a previous qualitative test, and developed it into a quantitative method for the determination of Ferric Iron with Stannous Chloride. In this method the Iron as Ferric Chloride is titrated with Stannous Chloride, while hot, until it becomes colorless. As stated previously, this change in color is not a sharp one, so for analytical purposes it is desirable to run over the end-point and back titrate with a standardized Iodine solution. Due to the rapid change in the reducing power of the Stannous solution, it is necessary to compare it with the Iodine solution at the same time that the Iron is being determined.

Scott⁶⁶ gives a modification of this method for small amounts of Iron, using a much weaker solution and performing the actual titration rapidly in a casserole to better observe the end-point. He also describes a rather complicated arrangement of apparatus for the purpose of preventing oxidation of the solution, by the use of which it is claimed, that it is not necessary to standardize oftener than once every ten or fifteen days.

64. C. Meincke, Z. Offentl. Chem., 4,433 (1898)

65. W. Fresenius, Z. anal. Chem., 25,160 (1886)

66. W. W. Scott, Stand. Meth. 4th Ed., 260 (1927)

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- 64. C. 4, 443 (1963)
- 65. W. 43, 150 (1963)
- 66. W. 43, 150 (1963)

Schimpf⁶⁷ includes a method for the determination of Mercuric Chloride among the uses of Stannous Chloride, which he refers to as the method of Laborde. This method consists of titrating a solution of the Mercuric Chloride, the pH of which has been accurately adjusted by a mixture of Acetic Acid and Ammonium Acetate, with the Stannous solution until a brownish color is obtained. The Stannous Chloride previously must have been standardized by titrating samples of known purity. While this author includes it as if it were of some importance, no references to such a method could be found elsewhere in the various books on Analytical Chemistry.

Muller and Gorne⁶⁸ have collected the available methods which could be used for the determination of Stannous Chloride, as well as those in which it is the standard solution itself, and investigated them potentiometrically, publishing their results in an article with the title "Potentiometrische Stannometrie". By the use of the potentiometer he was able to eliminate the color change as a source of error, as well as to increase the accuracy of the methods to some extent. He found that he could obtain satisfactory results when Stannous Chloride reacted with Ferric Chloride, Iodine, Potassium Permanganate, Potassium Bichromate, and Mercuric Perchlorate. He was unable to obtain any results with Potassium Ferricyanide, and not very satisfactory ones with Gold and Platinum in the

67. H. W. Schimpf, *Ess. of Vol. Anal.* 4th Ed., 231 (1925)

68. E. Muller and W. Gorne, *Z. anal. Chem.*, 73, 385 (1928)

form of their complex Chlorine Acids. In a later paper, with Bennewitz,⁶⁹ he published more of his work with these two latter substances, but further improvements will have to be made before these methods will be useful.

Stannous Chloride solutions, like those of Titanous and Ferrous salts, are very unstable. When it is desired that the reducing value of the solution should remain constant, it is necessary to take precautions to prevent oxidation. Among those recommended are the keeping of the solution under an atmosphere of Hydrogen from a Kipp generator, and the use of yellow Phosphorous or Pyrogalllic Acid for the purpose of removing the Oxygen from the air. As all of these require bulky and complicated pieces of apparatus, the oxidation of Stannous Chloride has been investigated by several workers, but thus far no definite recommendations have resulted from their efforts.

69. E. Muller and R. Bennewitz, Z. anorg. Chem., 179, 113 (1929)

Chapter IV

STANNOUS PERCHLORATE

A very extensive survey of the literature revealed but two references to this substance, one by Noyes and Toabe,⁷⁰ who prepared it, in solution, as a preliminary to their investigation of the electrode potential of Stannous Tin, and a second by Prytz,⁷¹ who made use of it during an investigation of the hydrolysis of the Stannous salts.

The most obvious method of preparation of this substance is to treat Tin with Perchloric Acid. Tin, in various forms, was treated with Perchloric Acid of various strengths, but in no case was an appreciable amount of the metal dissolved after four or five hours of continued heating. Letters were then written to two men who had worked on Perchlorates for possible information not otherwise available. Dr. G. F. Smith of the University of Illinois replied that he had never prepared any of this salt, but that he would try to do so. In a later letter he stated that very fine turnings would react slowly if heated with 70% Perchloric Acid. Dr. Stephen Popoff of the State University of Iowa suggested the treatment of Stannous Chloride with Silver Perchlorate. As none of the latter substance was available, this method could not be tried out.

Due to the non-volatility of Perchloric Acid, it seemed

70. A. A. Noyes and K. Toabe, J. Am. Chem. Soc., 39, 1537 (1917)

71. M. Prytz, Z. anorg. allgem. Chem., 172, 147 (1928)

Chapter IV

STANDARD PRACTICES

A very extensive survey of the literature revealed but two papers on this subject, one by H. H. H. and one by H. H. H. In addition, as a preliminary to the investigation of the electrochemical potential of hydrogen, and a second by H. H. H. who made use of it during an investigation of the hydrolysis of the hydrogen salts.

The most common method of preparation of this substance is to treat the hydrogen with sulfuric acid. This is various forms, and is treated with sulfuric acid of various strengths, but in

no case was an equivalent amount of the acid dissolved after treatment of the substance with sulfuric acid. In some cases

even treated with two and worked on the substance for some time, but no other information was obtained. Dr. H. H. H.

of the University of Illinois reported that he had never been able to obtain this salt, but that he would try to do so. In

a letter I had he stated that very fine crystals would result if treated with 50% sulfuric acid. Dr. H. H. H.

of the State University of Iowa suggested the treatment of hydrogen chloride with silver chloride. In none of the

other substances was mentioned, and it is possible that the

One to the non-solubility of hydrogen chloride, it is not

reasonable to expect that if Stannous Chloride was evaporated with it, Stannous Perchlorate would result and Hydrogen Chloride would be given off. Several attempts to do this were made, but in every case yellowish muddy suspensions were obtained before the fumes of Perchloric Acid started to come off. A qualitative test with Silver Nitrate solution showed considerable Chloride present so this method was abandoned.

It was suggested that the salt could be made by the reaction between Stannous Hydroxide and Perchloric Acid. All the available samples of Stannous Chloride were dissolved in Hydrochloric Acid, and carefully neutralized with Sodium Hydroxide solution. The resulting precipitate was filtered and washed with warm water, but after numerous (in one case seventeen) washings, the material still contained Chlorides. As a result, this method was abandoned, also.

Noyes and Toabe^{*} had worked out an indirect method which they found to be successful. This method consisted of first forming Cupric Perchlorate by treating Cupric Oxide with the acid, and then displacing the Copper by Tin to form the Stannous salt. After a few preliminary experiments, this procedure was followed, but the resulting solution had a brownish scum and gave a very decided test for Iron. After obtaining Copper Oxide and Tin of better grade, carefully distilling the water, and carrying out the displacement in a closed container, a satisfactory material (in solution) was obtained.

*. See Ref. 70, page 29

The following method was finally used. 32 grams of Copper Oxide were added to 110cc. of 60% Perchloric Acid(sp.gr. 1.54) which had previously been diluted to 400cc. and the mixture heated to boiling. In a short time, a clear blue solution was obtained, which was then cooled and poured into a glass stoppered bottle of about 450cc. capacity, containing 100g. of 60 mesh Tin. This was shaken vigorously by hand, for fifteen minutes, and then occasionally during the next two days, but allowed to stand tightly stoppered during the interval between shakings. By the morning of the fourth day, no test for Copper could be obtained with Ammonium Hydroxide, so the solution was filtered thru glass wool into a bottle containing Tin. An attempt to substitute mechanical stirring resulted in a rather dirty turbidity which was probably due to the presence of very finely divided Copper or Tin. In a few days a yellow coloration developed, but as the authors of this method had found this to have no undesirable effect, this was not considered detrimental. This solution when first prepared was 2.08 Normal and since the volume was 390cc. the yield, based on the Cupric Oxide, was practically quantitative. All solutions used in titrations were prepared by merely diluting this solution to the desired strength.

It was originally intended that this substance should be substituted for the Chloride, so, as the chief drawback to the latter is its lack of stability, experiments intended to

The following method was finally used. 25 grams of copper
peroxide were added to a solution of 500 peroxide in 100 ml.
of water. The solution was then stirred for 24 hours. The
solution was then filtered. In a test tube, a clear blue
solution was obtained, which was then heated and poured into
a glass beaker. The solution was then stirred for 24 hours.
The solution was then filtered. This was done repeatedly by hand.
The solution was then filtered and then concentrated by heating the test
tube, but allowed to stand until nearly evaporated before the next
step was taken. In the morning of the 10th day, the
solution was filtered and then concentrated with a water bath.
The solution was then filtered and then concentrated into a small
volume. An attempt was made to concentrate the solution by
evaporating it in a test tube, but this was not possible due to
the presence of very fine particles of copper or tin. In a few
days a yellow solution developed, but as the solution was
reduced and found this to have no undesirable effect, this was
not concentrated further. The solution was then reduced
with 2.5% formal and then the volume was reduced to 10 ml.
based on the original oxide. The solution was then reduced
with 2.5% formal and then the volume was reduced to 10 ml.
The solution was then reduced and then the volume was reduced to 10 ml.
It was originally intended that this solution should be
evaporated to the dry state, but as the solution was found to
be stable in the lack of stability, experiments were made

measure the stability of the Perchlorate in the usual strengths used in analysis were made. At the same time solutions of the Chloride were measured similarly.

The first method which was tried was an attempt to measure the absorption of the Oxygen by the change in pressure in a closed flask by means of a Mercury manometer. It was found that both solutions absorbed the gas at a very rapid rate, so great, in fact, that no satisfactory quantitative results could be obtained.

A method making use of the change of electromotive force caused by the oxidation was then substituted. After a number of preliminary measurements were made, three sets of values were obtained which resembled each other enough to be compared. The average of each reading is given in Table I, and the data is plotted in Fig. 4. From these results, it can be seen that the stability of the Perchlorate is not much, if any, better than that of the Chloride.

In the meantime, a series of experiments were carried out in order to ascertain if Stannous Perchlorate possessed any particular properties which would make it desirable as a reducing agent. Each one of these will be considered in the following pages.

TABLE I
COMPARATIVE STRENGTHS
 of
STANNOUS PERCHLORATE and STANNOUS CHLORIDE

As Determined from Measurements of Electromotive Force

Time in Hours	E. M. F. in Volts			
	Perchlorate		Chloride	
	1.0 N	0.1 N	1.0 N	0.1 N
0.0	.0284	-.0450	.0425	-.0636
0.5	.0336	-.0407	.0445	-.0515
1.0	.0445	-.0190	.0515	-.0404
2.0	.0477	-.0111	.0548	-.0190
3.0	.0534	.0000	.0547	-.0138
4.0	.0562	.0195	.0674	.0000
5.0	.0618	.0210	.0727	.0307
6.0	.0663	.0210	.0746	.0304
7.0	.0614	.0241	.0733	.0324
24.0	.0630	.0210	.0862	.0325

The Tenth Normal Calomel and bright Platinum electrodes were used for these determinations. The same electrodes were used for all solutions.

TABLE I

DATA-1210-1210-1210STATIONARY PERMANENT AND STATIONARY PERMANENT

As determined from measurements of atmospheric pressure

Time in Hours		Time in Hours		Time in Hours	
Stationary		Stationary		Stationary	
0.0	0.0	0.0	0.0	0.0	0.0
0.1	0.1	0.1	0.1	0.1	0.1
0.2	0.2	0.2	0.2	0.2	0.2
0.3	0.3	0.3	0.3	0.3	0.3
0.4	0.4	0.4	0.4	0.4	0.4
0.5	0.5	0.5	0.5	0.5	0.5
0.6	0.6	0.6	0.6	0.6	0.6
0.7	0.7	0.7	0.7	0.7	0.7
0.8	0.8	0.8	0.8	0.8	0.8
0.9	0.9	0.9	0.9	0.9	0.9
1.0	1.0	1.0	1.0	1.0	1.0
1.1	1.1	1.1	1.1	1.1	1.1
1.2	1.2	1.2	1.2	1.2	1.2
1.3	1.3	1.3	1.3	1.3	1.3
1.4	1.4	1.4	1.4	1.4	1.4
1.5	1.5	1.5	1.5	1.5	1.5
1.6	1.6	1.6	1.6	1.6	1.6
1.7	1.7	1.7	1.7	1.7	1.7
1.8	1.8	1.8	1.8	1.8	1.8
1.9	1.9	1.9	1.9	1.9	1.9
2.0	2.0	2.0	2.0	2.0	2.0

The data were obtained from the stationery permanent and stationary permanent stations. The data were obtained from the stationery permanent and stationary permanent stations. The data were obtained from the stationery permanent and stationary permanent stations.

FIGURE IV

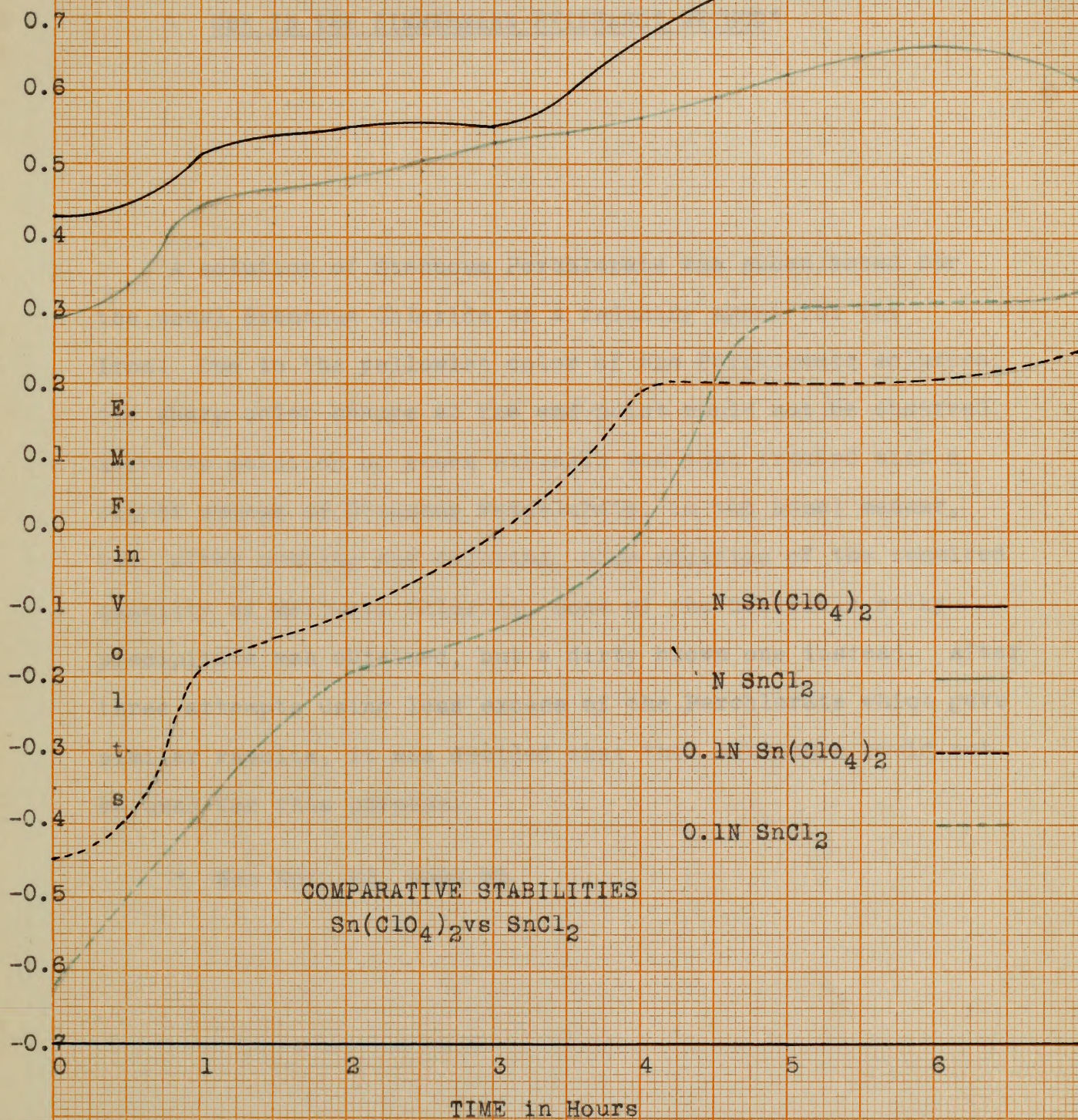


FIGURE IV

COMPARATIVE STABILITIES
 $\text{Sn}(\text{ClO}_4)_2$ vs SnCl_2

0.1N SnCl_2

0.1N $\text{Sn}(\text{ClO}_4)_2$

N SnCl_2

N $\text{Sn}(\text{ClO}_4)_2$

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USE IN THE ZIMMERMANN-REINHARDT METHOD*

A solution of Stannous Perchlorate was substituted for the usual Stannous Chloride as a reducing agent for the Iron. Due to the yellowish color of the Perchlorate solution, the sharp color change at the end-point could not be observed. A Ferric solution of known strength was then treated with a slight excess of Stannous Perchlorate, in the usual manner, but, after cooling and diluting, upon addition of the required quantity of Mercuric Chloride, none of the desirable silky precipitate was obtained, but a dirty brown one instead. After three attempts using less excess of the Perchlorate which gave similar results, it was decided that this substance could not be used for this purpose.

* See Ref. 63, page 25

A solution of aluminum perchlorate was substituted for
the usual aluminum chloride as a reducing agent for the
iron. Two of the yellowed color of the perchlorate solution,
the same color change as the red color could not be observed.
A white solution of iron was then prepared with a
slight excess of aluminum perchlorate, in the usual manner,
but, after cooling and filtering, upon addition of the powdered
quantity of barium chloride, none of the characteristic
precipitate was obtained, but a dirty brown one resulted. A test
with litmus, which gave excess of the perchlorate which was
made, was decided that this substance could not
be used for this purpose.

USE AS A QUALITATIVE REAGENT

Most of the modern systems of Qualitative Analysis determine the presence of Mercuric Mercury by its reaction with Stannous Chloride. In this test a white precipitate of Mercurous Chloride is first formed, which in the presence of an excess of the Stannous salt, darkens rapidly due to the further reduction to metallic Mercury.

A solution of the Perchlorate was prepared of the same strength as that of the usual Chloride solution, but upon being added to a solution of Mercurous Chloride, the white precipitate first formed dissolved instead of darkening, probably due to the oxidizing power of the Perchloric Acid present. It would seem that from this behavior, that the Perchlorate is not suitable for use as a qualitative reagent.

USE AS A QUALITATIVE REAGENT

Most of the modern systems of qualitative analysis determine the presence of metallic elements by the reaction with stannous chloride. In this test a white precipitate of stannous chloride is first formed, which is the evidence of an excess of the stannous salt, whereas usually it is the reverse reaction to metallic mercury.

A solution of the perchlorate was prepared by the same strength as that of the usual chloride solution, but was being added to a solution of stannous chloride, the white precipitate first formed dissolved instead of increasing, probably due to the oxidizing power of the perchloric acid. It would seem that this behavior, that the perchlorate is not suitable for use as a qualitative reagent.

Table II

STANNOUS PERCHLORATE vs IODINE

Procedure:-25cc. of Iodine solution(.09588N) was diluted to 400cc. with distilled water, Perchloric Acid(20%) was added, and titrated with an approximately 0.1N solution of Stannous Perchlorate. The course of the reaction was followed by the potentiometer using the electrodes previously described.

Volume added in cc.	E. M. F. in volts		
	5cc. Acid	8cc. Acid	10cc. Acid
0	.3640	.3618	.3546
5	.3470	.3429	.3424
10	.3325	.3315	.3295
15	.3172	.3179	.3164
20	.3014	.2950	.2754
23	.2837	.0301	.0234
25	.0087	.0153	.0123
27	.0000	.0096	.0085
30	-.0107	.0036	.0050
35	-.0153	-.0050	.0020
40	-.0177	-.0086	-.0062

Remarks:-In all three concentrations of acid, an end-point was obtained at practically 23.0cc., as shown by the color change and the drop in potential. The color of the Starch was reddened by the solution.

Conclusion:-Stannous Perchlorate reduces Iodine quantitatively.

Table II

STANDARD REDOX POTENTIALS

Procedure: A 100 ml. of 0.1M solution (0.055M) was added to 50 ml. of distilled water. Potassium dichromate (0.05M) was added and the solution was made up to 100 ml. The course of the reaction was followed by the potentiometer using an electrode assembly described.

Volts in cell	Volts in cell	Volts in cell	Volts in cell
0.00	0.00	0.00	0.00
0.01	0.01	0.01	0.01
0.02	0.02	0.02	0.02
0.03	0.03	0.03	0.03
0.04	0.04	0.04	0.04
0.05	0.05	0.05	0.05
0.06	0.06	0.06	0.06
0.07	0.07	0.07	0.07
0.08	0.08	0.08	0.08
0.09	0.09	0.09	0.09
0.10	0.10	0.10	0.10
0.11	0.11	0.11	0.11
0.12	0.12	0.12	0.12
0.13	0.13	0.13	0.13
0.14	0.14	0.14	0.14
0.15	0.15	0.15	0.15
0.16	0.16	0.16	0.16
0.17	0.17	0.17	0.17
0.18	0.18	0.18	0.18
0.19	0.19	0.19	0.19
0.20	0.20	0.20	0.20

Remarks: In all cases concentrations of acid, as indicated, were obtained at pH 0.0. The pH of the solution was checked by the potentiometer.

Conclusion: Standard redox potentials for the various reactions.

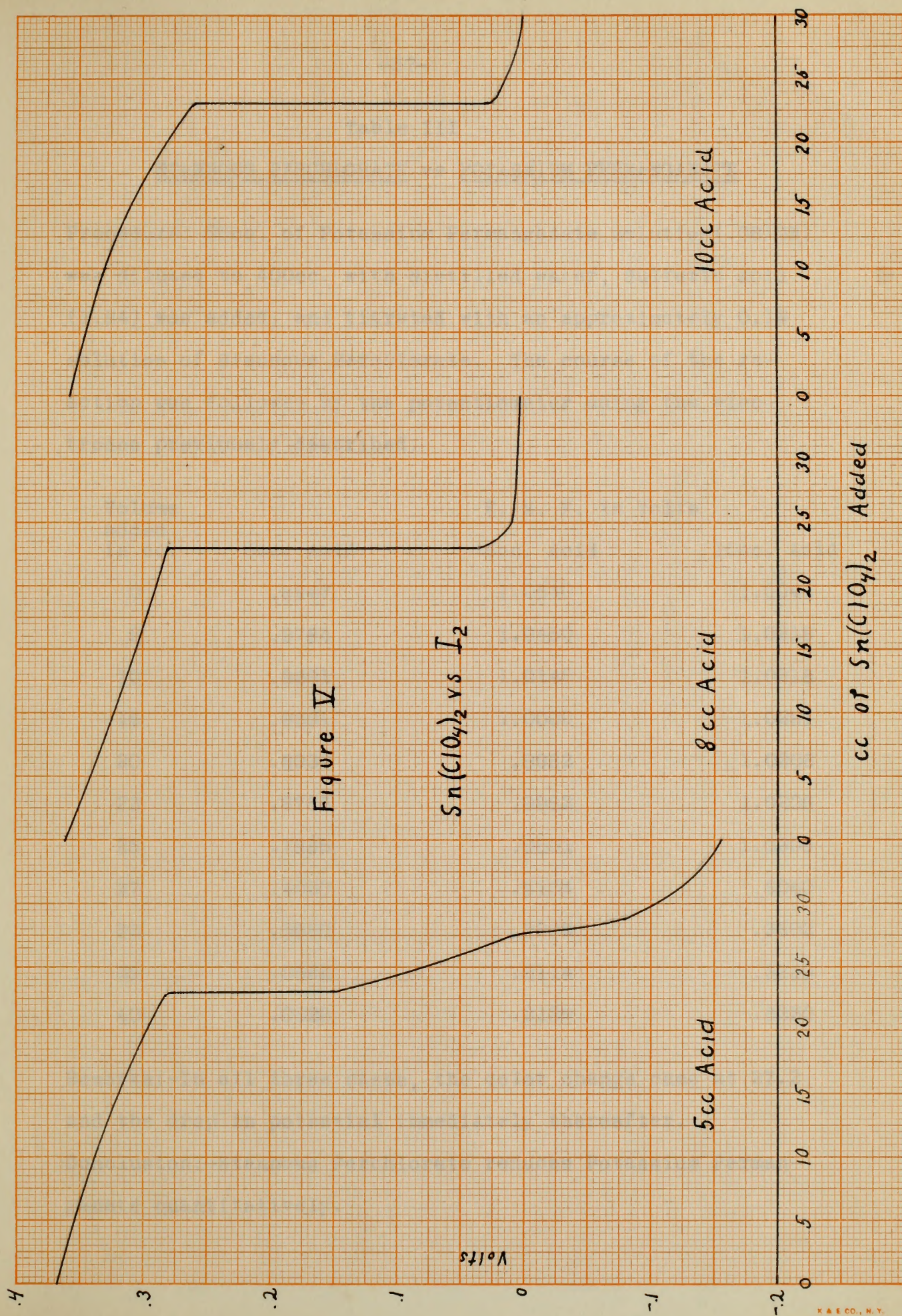


Table III

STANNOUS PERCHLORATE vs POTASSIUM PERMANGANATE

Procedure:-25cc. of Potassium Permanganate solution(.0819N) was diluted to 400cc. with distilled water, Sulfuric Acid (1.84) was added, and titrated with an approximately 0.1N solution of Stannous Perchlorate. The course of the reaction was followed by the potentiometer using the electrodes previously described.

Volume added in cc.	E. M. F. in Volts		
	5cc. Acid	8cc. Acid	10cc. Acid
0	.8947	1.0640	1.0041
5	.9784	1.0450	1.0218
10	.9391	1.0140	1.0218
15	.9391	1.0000	1.0221
20	.8939	.9982	1.0206
23	.8766	.9982	1.0206
25	.7885	.9801	1.0206
27	.4000	.5104	.6040
30	.0680	.2203	.3502
35	.0662	.2114	.3230
40	.0628	.2125	.3230

Remarks:-In all three cases, the color change came at 27.2 and the drop in potential immediately thereafter.

Conclusion:-Stannous Perchlorate reduces Potassium Permanganate quantitatively.

Table III

STANNOUS PEROXIDE - POTASSIUM PERMANGANATE

Procedure: 2500.0 g. of stannous peroxide (99.9% pure) was added to 4000.0 g. of distilled water. Sulfuric acid (1.25) was added, and filtered with an engine nozzle. A solution of potassium permanganate was added. The volume of the solution was reduced by the potentiometer using the above procedure previously described.

Volume of 0.1% KMnO ₄ solution	Volume of 0.1% SnO ₂ solution	Volume of 0.1% H ₂ SO ₄ solution
0	1.000	1.000
5	1.000	1.000
10	1.000	1.000
15	1.000	1.000
20	1.000	1.000
25	1.000	1.000
30	1.000	1.000
35	1.000	1.000
40	1.000	1.000
45	1.000	1.000
50	1.000	1.000
55	1.000	1.000
60	1.000	1.000
65	1.000	1.000
70	1.000	1.000
75	1.000	1.000
80	1.000	1.000
85	1.000	1.000
90	1.000	1.000
95	1.000	1.000
100	1.000	1.000

Remarks: In all three cases, the color change came at 25.0 ml. of 0.1% KMnO₄ solution. The color change was immediately characteristic. Conclusion: Stannous peroxide reduces potassium permanganate quantitatively.

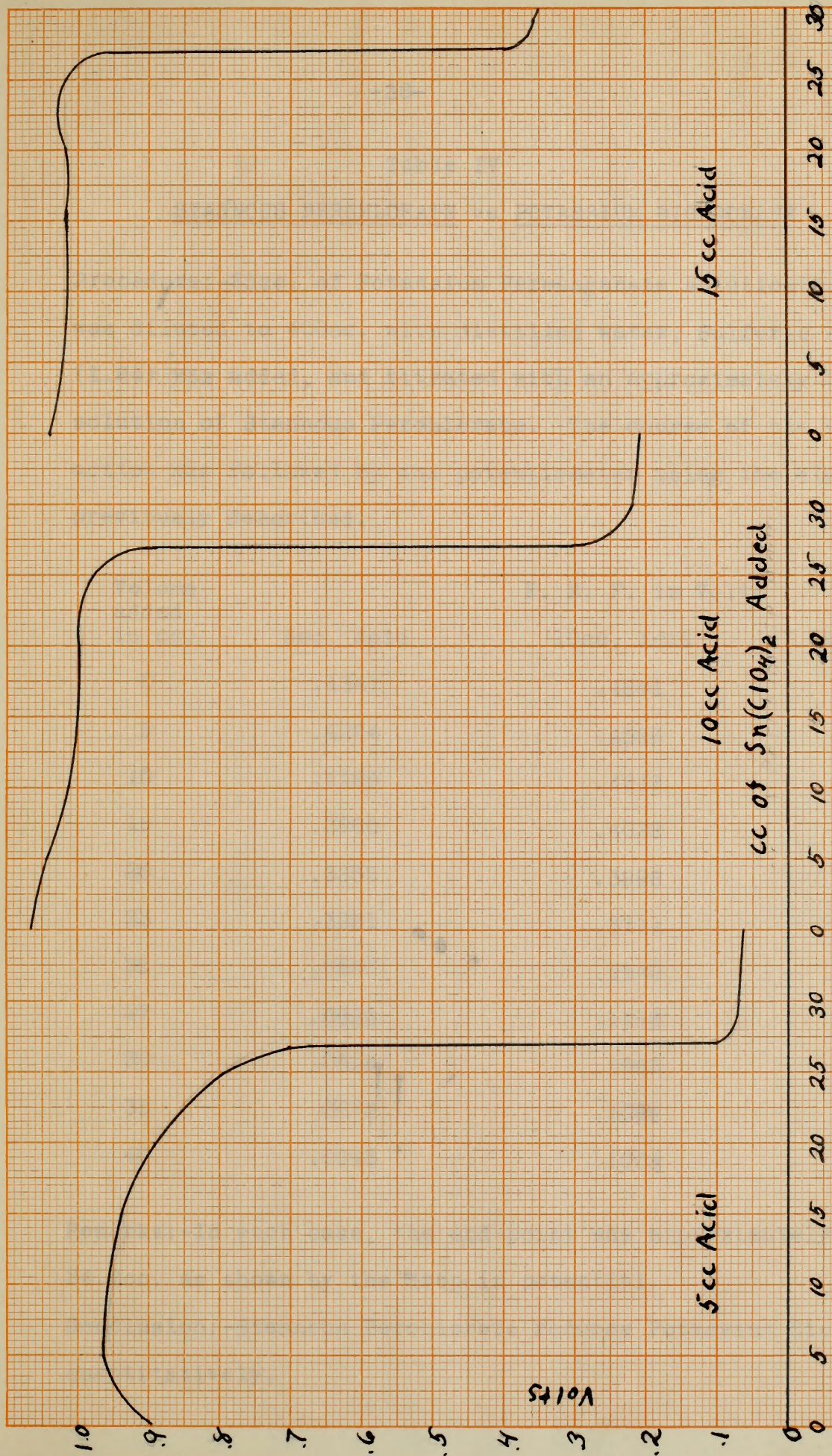


Figure VI

$\text{Sn}(\text{ClO}_4)_2$ vs KMnO_4

Table IV

STANNOUS PERCHLORATE vs POTASSIUM BICHROMATE

Procedure:-25cc. of Potassium Permanganate solution(0.100N) was diluted to 400cc. with distilled water, Sulfuric Acid (1.84) was added, and titrated with an approximately 0.1N solution of Stannous Perchlorate. The course of the reaction was followed by the potentiometer using the electrodes previously described.

Volume added in cc.	E. M. F. in Volts		
	5cc. Acid	10cc. Acid	15cc. Acid
0	.4341	.4841	.5730
5	.4274	.4588	.5626
10	.4169	.4316	.5577
15	.3900	.4028	.5326
20	.3855	.3898	.4094
23	.3251	.3111	.3055
25	.0680	.1130	.0703
27	.0638	.1116	.0619
30	.0618	.1092	.0440
35	.0672	.1088	.0319
40	.0643	.1008	.0327

Remarks:-In each case, the end-point was approximately at 24.7cc. as shown by the drop in potential.

Conclusion:-Stannous Perchlorate reduces Potassium Bichromate quantitatively.

STANDARDIZATION OF POTASSIUM BICHROMATE

Procedure:—A known weight of potassium bichromate is dissolved in distilled water, sulfuric acid is added, and the solution is titrated with an approximately 0.1N solution of ferrous sulfate. The volume of the ferrous sulfate solution required is determined by the potentiometer using the electrode previously described.

Vol. of 0.1N FeSO ₄	Sec. Vol.	10cc. Acid	Vol. of 0.1N FeSO ₄
0	4.361	4.361	0.000
5	4.375	4.375	0.005
10	4.388	4.388	0.010
15	4.400	4.400	0.015
20	4.412	4.412	0.020
25	4.424	4.424	0.025
30	4.436	4.436	0.030
35	4.448	4.448	0.035
40	4.460	4.460	0.040
45	4.472	4.472	0.045
50	4.484	4.484	0.050
55	4.496	4.496	0.055
60	4.508	4.508	0.060
65	4.520	4.520	0.065
70	4.532	4.532	0.070
75	4.544	4.544	0.075
80	4.556	4.556	0.080
85	4.568	4.568	0.085
90	4.580	4.580	0.090
95	4.592	4.592	0.095
100	4.604	4.604	0.100

Remarks:—In this case, the weight of potassium bichromate is 0.1000 g. as shown by the drop in potential.

Concentration:—Standard Potassium Bichromate

Qualitatively.

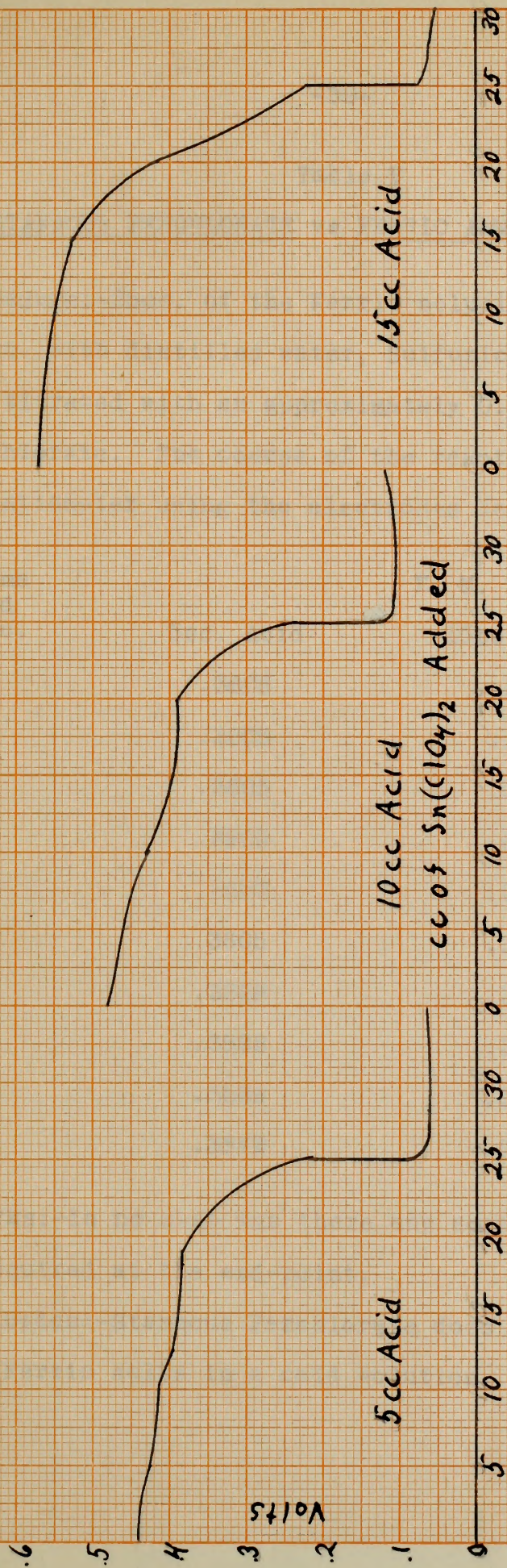


Figure VII

Sn(IV)_2 vs $\text{H}_2\text{Cr}_2\text{O}_7$

Table V

STANNOUS PERCHLORATE vs FERRIC AMMONIUM SULFATE (Cold)

Procedure:-25cc. of the Ferric solution(1.0) was diluted to 400cc. with distilled water, Sulfuric Acid(1.84) was added, and titrated with an approximately 0.1N solution of Stannous Perchlorate. The course of the reaction was followed by the potentiometer using the electrodes described previously.

Volume added in cc.	E. M. F. in Volts		
	5cc. Acid	10cc. Acid	15cc. Acid
0	.3605	.3752	.3786
5	.3605	.3733	.3685
10	.3605	.3729	.3662
15	.3605	.3710	.3668
20	.3605	.3671	.3668
23	.3605	.3670	.3635
25	.3588	.3590	.3635
30	.3588	.3485	.3635
35	.3588	.3328	.3326
40	.3572	.3063	.3000

Remarks:-in no case was there any apparent change in potential as required at the end-point.

Conclusion:-Stannous Perchlorate does not react quantitatively with Ferric salts in a cold solution.

Table 1

STANDARD DEVIATION OF THE TITRATION ERROR

Preparation: 100 ml. of the 0.1N solution (1.0) was added to 400 ml. of distilled water, adjusted with 0.1N solution of potassium permanganate. The volume of the solution was 1 liter and the concentration was 0.025N. The standard deviation was 0.001.

Volume added in cc.	0.1N Acid	0.025N Acid	0.01N Acid
0	0.000	0.000	0.000
5	0.005	0.005	0.005
10	0.010	0.010	0.010
15	0.015	0.015	0.015
20	0.020	0.020	0.020
25	0.025	0.025	0.025
30	0.030	0.030	0.030
35	0.035	0.035	0.035
40	0.040	0.040	0.040

Standard deviation of the titration error

Standard deviation of the titration error

Standard deviation of the titration error

Standard deviation of the titration error

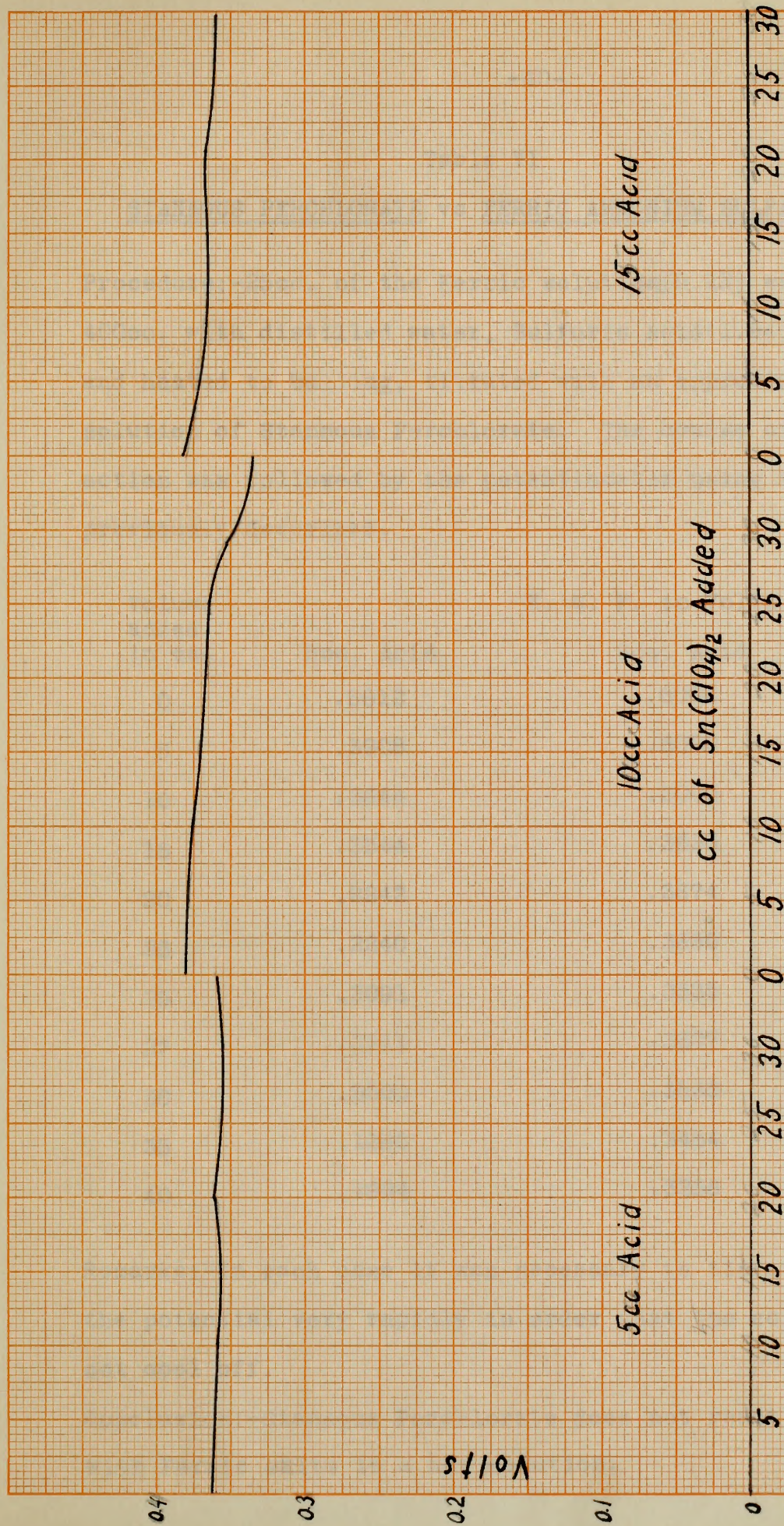


Figure VIII

$\text{Sn}(\text{ClO}_4)_2$ vs $\text{FeNH}_4(\text{SO}_4)_2$ (cold)

Table VI

STANNOUS PERCHLORATE vs FERRIC AMMONIUM SULFATE (Hot)

Procedure:-25cc. of the Ferric solution(0.1N) was diluted to 400cc. with distilled water, Sulfuric Acid(1.84) was added, and heated to boiling, titrated with an approximately 0.1N solution of Stannous Perchlorate. The course of the reaction was followed by the potentiometer using the electrodes previously described.

Volume added in cc.	E. M. F. in Volts		
	5cc. Acid	8cc. Acid	10cc. Acid
0	.5912	.6064	.6304
5	.3908	.3000	.4114
10	.3644	.3000	.3968
15	.2344	.3835	.3753
20	.2242	.3674	.3514
23	.2240	.3680	.3307
25	.2091	.3535	.3295
27	.2111	.3607	.3142
30	.2000	.3535	.2925
35	.1880	.3454	.2838
40	.1994	.3258	.2818

Remarks:-In each case it was necessary to titrate and read the potential very rapidly in order that the solutions might not cool off.

Conclusion:-Stannous Perchlorate does not react quantitatively with Ferric salts in a hot solution.

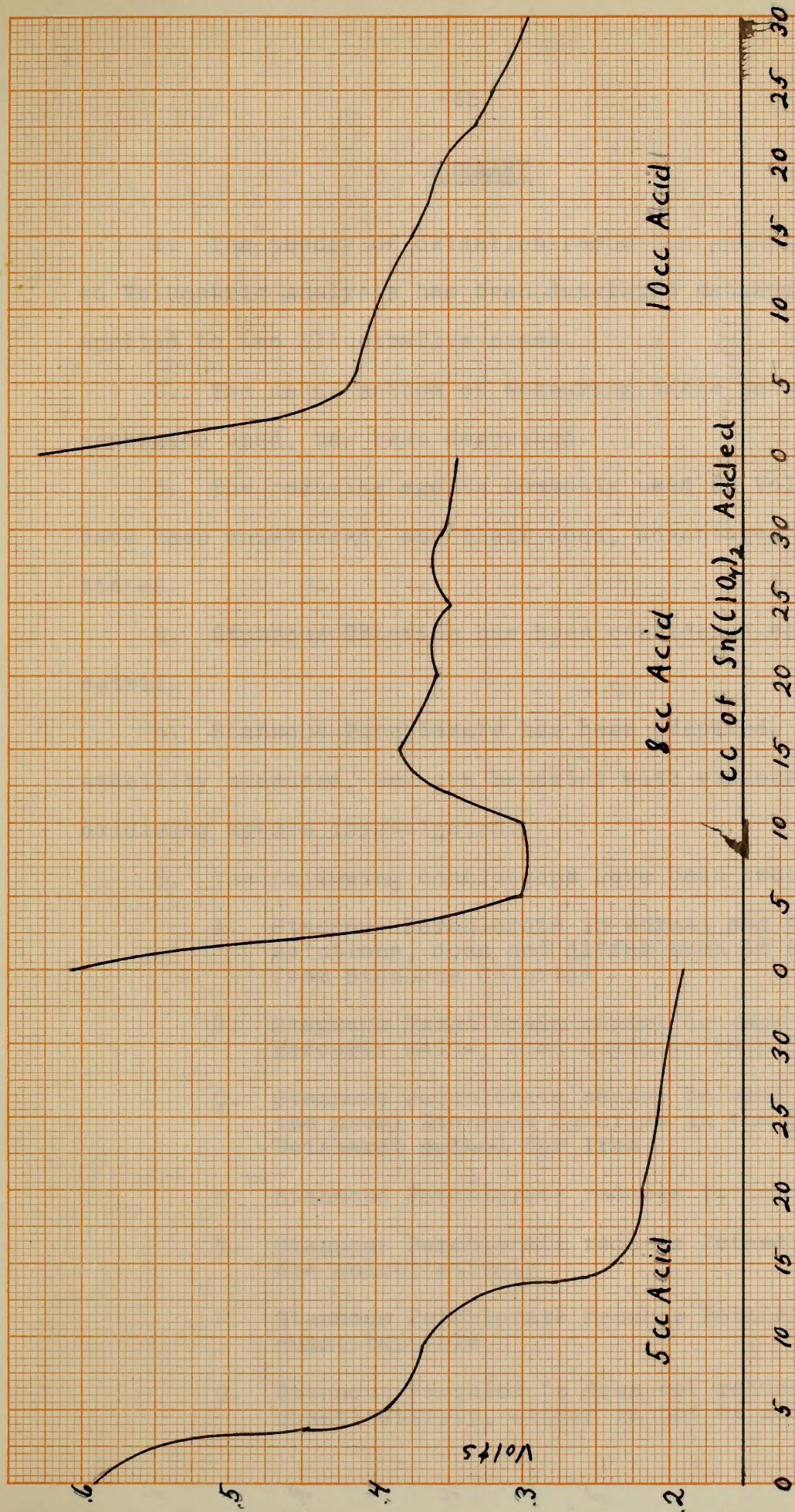


Figure IX

$\text{Sn}(\text{ClO}_4)_2$ vs $\text{FeNH}_4(\text{SO}_4)_2$ (Hot)

SUMMARY

1. The theory of oxidation-reduction potentials as related to Volumetric Analysis has been developed mathematically, and applied to two illustrative cases.

2. The usual method of measuring these potentials, and the apparatus used, has been described.

3. The reducing agents commonly used in Volumetric Analysis have been considered, and their uses, advantages and objections stated.

4. Stannous Chloride has been considered somewhat more in detail.

5. Stannous Perchlorate has been prepared, its comparative stability measured, and its behavior with various commonly used oxidizing agents investigated.

6. The following conclusions have been reached:

- A. Stannous Perchlorate in normal and tenth normal solutions, does not differ much in stability from Stannous Chloride
- B. Stannous Perchlorate cannot be used to test for Mercuric salts, even qualitatively
- C. Stannous Perchlorate cannot be used in place of the usual Stannous Chloride in the Zimmermann-Reinhardt method for Iron
- D. Stannous Perchlorate reduces Iodine quantitatively
- E. Stannous Perchlorate reduces Potassium Permanganate quantitatively
- F. Stannous Perchlorate reduces Potassium Bichromate quantitatively
- G. Stannous Perchlorate does not reduce Ferric salts quantitatively, either in hot or cold solution

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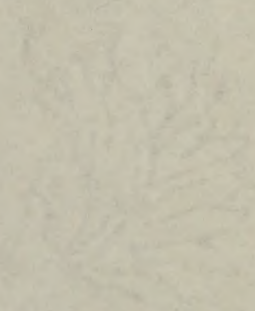
ABBREVIATIONS

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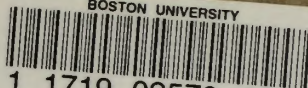
ABSTRACTS

All publications used in the above bibliography and in the
 foot notes are published in the following order:
 1. The International Union of Pure and Applied Chemistry and
 2. The official journal of the International Union of Pure and Applied
 Chemistry, published by the International Union of Pure and Applied Chemistry, 1923.



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